

Comparing the value of bioproducts from different stages of anaerobic membrane bioreactors

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Abstract

The anaerobic digestion process in anaerobic membrane bioreactors is an effective way for Waste Management, energy sustainability and pollution control in the environment. This digestion process basically involves the production of volatile fatty acids and biohydrogen as intermediate products and methane as a final product. This paper compares the value of bioproducts from different stages of anaerobic membrane bioreactors through a thorough assessment. The value was assessed in terms of technical feasibility, economic assessment, environmental impact and impact on society. Even though the current research objective is more inclined to optimize the production of methane, the intermediate products could also be considered as economically attractive and environment friendly options. Hence, this is the first review study to correlate the idea into an anaerobic membrane bioreactor which is expected to guide future research pathways regarding anaerobic process and its bioproducts.

Keywords: Anaerobic membrane bioreactors, bioproducts, volatile fatty acids, biohydrogen, methane, assessment

1. Introduction

Recovering resources and energy from wastes and wastewater is deemed to be of primary interest for environmental engineers and researchers. Both aerobic and anaerobic processes have been utilized to design membrane bioreactors for industrial wastewater treatment (Falahti-Marvast and Karimi-Jashni, 2015; Ma (D.) et al., 2016). Of these two, the anaerobic membrane bioreactors (AnMBRs) are considered to be a good, low cost alternative that has the advantage of less energy requirement (Pretel et al., 2016), high organic loading rate (OLR), bioenergy and nutrient recovery (Chan et al., 2009). AnMBR is an integrated system where a low pressure microfiltration/ultrafiltration membrane module is coupled with an anaerobic bioreactor. The membrane module separates liquid from biomass and increases biomass concentration. Biogas is generated through anaerobic digestion process in the bioreactor and the filtered liquid from membrane module is collected as permeate (Chang, 2014). Fig. 1 shows a simplified schematic diagram of anaerobic bioreactor with two major configurations.

Fig. 1

Till now, the industrial application of AnMBRs is limited as it requires a larger membrane area and intensive biogas recycling that contribute to the operation and maintenance costs (Ozgun et al., 2013; Shin et al., 2014). Since the process offers the prospect of energy recovery, studies have focused on an optimization protocol for maximum methane production from the final stage (Mei et al., 2016). Although it is a much needed initiative to mitigate the growing energy crisis, the environmental impact of the product is one that contributes to greenhouse gas emissions. Experiments have already proven the technical feasibility to extract intermediate products like biohydrogen and volatile fatty acids (VFAs) from the

individual anaerobic digestion process (Abdelsalam et al., 2016; Guwy et al., 2011; Yuan and Zhu, 2016). The current AnMBR models designed to produce methane have a number of limitations in terms of economic feasibility and sustainable energy production (Lin et al., 2011; Pretel et al., 2014; Pretel et al., 2015). The purpose of extracting VFAs and biohydrogen over methane production is governed by two main reasons. Firstly, VFA has already been identified as a suitable precursor for biopolymers and reduced chemicals of high value, such as alcohols, aldehydes, ketones, esters and biofuels (Scoma et al., 2016). Secondly, as a fuel, biohydrogen has a high energy density (Higher Heating Value of 142MJ/Kg compared to 55 MJ/kg of methane) and the combustion product (H_2O) is environmentally friendly (Guwy et al., 2011; Kim et al., 2016). Therefore, the technical and economic feasibility study for AnMBRs designed to extract these intermediate products can be a promising aspect to improve the economic feasibility of AnMBR.

The objective of this study is to provide a brief comparison between the value of the bioproducts from AnMBRs, i.e. VFAs, biohydrogen, and methane. To support the comparison under different operating conditions, technical feasibility has been studied during simultaneous and individual production of different AnMBRs products. The technical overview is followed by an economic assessment that includes the potential for each product and the costs involved in different AnMBRs' operating conditions and arrangements. Finally, to support the aim of the comparison, each component's environmental and societal impact was discussed.

2. Technical Overview

2.1. The Anaerobic Digestion Process

The anaerobic digestion (AD) is a reduction process with a number of biochemical reactions where microorganisms break down biodegradable materials under anoxic conditions (Adekunle and Okolie, 2015). The process involves four major phases: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. It begins with bacterial hydrolysis of insoluble organic materials and higher molecular mass compounds such as carbohydrates, proteins and fats into soluble derivatives like amino acids, sugars and fatty acids. Strict anaerobes such as clostridia, facultative bacteria, bacteroides are the major drivers of this stage (Adekunle and Okolie, 2015; Passos et al., 2014).

The hydrolyzed monomers produced in the first stage are then converted further into VFAs, alcohols, hydrogen and carbon dioxide by the acidogenic bacteria (Kim et al., 2010; Wei et al., 2015; Zhao et al., 2016). Among these products, VFAs and alcohols cannot be converted directly by the methanogens. The third stage involves the conversion of long-chain VFAs into acetate, hydrogen and carbon dioxide (Li (Y.) et al., 2015; Ozgun et al., 2013). Finally, intermediate products from the previous stages are converted into methane by the methanogens. Compared to the initial three phases, the biochemical reaction rate in this phase is the slowest (Lv et al., 2016; Passos et al., 2014). Fig.2 summarizes the major phases of anaerobic digestion process.

Fig. 2

2.2. Optimization of AD process

The growth rate of microorganisms in different stages varies widely according to their physiology, nutritional needs, temperature and pH sensitivity. The greatest challenge is to maintain a delicate balance between two major groups: the acid and the methane forming

microorganisms. Reactor instability and low methane yield are two predominant issues observed in modern anaerobic model (Adekunle and Okolie, 2015).

An efficient anaerobic digestion process requires the rate optimization for both initial hydrolysis and final methanogenesis processes. When the rate of hydrolysis is higher compared to the final methanogenesis stage, the produced VFA can accumulate in the system and result in decrease of pH in the reactor, which in turn can lead to the inhibition of the methanogenesis and induce system failure of the digester. Hence, controlling the rate of hydrolysis is important to prevent methanogenesis inhibition due to pH reduction in the system (Fezzani and Ben Cheikh, 2010; Xu et al., 2014). Besides being the slowest among the phases, methanogenesis is also sensitive to operating conditions like pH, VFAs/SCOD ratio, OLR, C/N ratio, retention time and the accumulation of ammonia and sulfide (Mao et al., 2015; Xu et al., 2014; Yuan and Zhu, 2016). As a result, methanogenesis is deemed to be the most vulnerable and performance limiting part of the anaerobic digestion. Since the current process optimization is based on maximum biogas production, all process operating conditions are tuned to increasing the performance of methanogenic archaea (Mao et al., 2015).

Several different parameters like pH, temperature, mixing, substrate, C/N ratio, and hydraulic retention time (HRT) are important for an optimum performance in the anaerobic process.

Although specific substrate properties and expected quality of the digestate define the operating conditions, parameters like values of temperature, pH and C/N ratio could be specified for generic anaerobic digestion models. Table 1 summarizes the most common operating ranges applied to create optimum AD performance.

Table 1

Both OLR and retention time depends on composition and type of waste that needs to be processed along with the model and arrangement of the bioreactors. From Table 1, it is evident that the process of methanogenesis and hydrolysis requires different production conditions and both phases have narrowed down the operating ranges that could be applied in AnMBR. Hence, wide and flexible operating ranges could be applied to AnMBR when the optimization of hydrolysis or acetogenesis is considered other than methanogenesis. So far, the current research on anaerobic processes provides only an incomplete picture because studies have been conducted under specific conditions. Only a few studies have provided a generic approach to optimize the AD process on AnMBR (Mei et al., 2016).

2.3. Advances made in methane production

Major fraction of research on anaerobic process has a common target, improvement of energy conversion efficiency through optimizing the anaerobic process for methane containing biogas production (Abdelsalam et al., 2016; Huang et al., 2016; Intanoo et al., 2015). To maximize the production of methane, the most recent research works include the tolerance of anaerobic digester under extreme operating conditions, for example high OLR (up to $40.0 \text{ kgCOD} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$), high salt concentration (up to 15 g/L sodium and 152 mg/L calcium concentration) and a wide range of pH values (from 6.2 to 8.5) (Xing et al., 2015; Yu et al., 2016). Among them, some experiments have already proved that the removal of intermediate products from anaerobic process (VFAs and biohydrogen) can enhance the methane yield from the final stage (Intanoo et al., 2015; Peces et al., 2016).

Currently, for methane production, one of the common performance management options includes the headspace flushing with N_2 and CO_2 where the increased CO_2 solubilization

relieves the O₂ stress on methanogenesis and results higher CH₄ yield (Koch et al., 2015). Experimental results from recycling the AD effluent also showed improved productivity of methane (Li (L.) et al., 2015). Additional common performance management options include adding cellulolytic organisms, optimizing substrate feeding frequency, and dosing nanoparticles etc. Some of the results include a rise upto 1.8 times methane production by adding 1–20 mg/L Co, Ni, Fe or Fe₃O₄ nanoparticles (Abdelsalam et al., 2016; Manser et al., 2015; Martin-Ryals et al., 2015).

Besides process optimization, recently developed idea such as the two-stage anaerobic digestion model provides the option for rate maximization by applying different operating conditions for hydrolysis/acidogenesis and methanogenesis. Intanoo et al. (2015) developed a two-stage AD process using upflow anaerobic sludge blanket reactor (UASB) that focuses on both producing hydrogen and methane from wastewater. Results from this experiment showed 39.83 l H₂/kg COD removal at a COD loading rate of 25 kg/m³d that refers more than 80% methane production compared to the production rate of 50-75% from a single stage anaerobic bioreactor.

Another option has been adding biogas AD accelerants to provide localized substrate concentration and favorable conditions for microbes (Mao et al., 2015). The research achievements in methane production clearly show a lot of promise. But economic feasibility assessment needs to be performed to compare the additional cost of multiple stage arrangement, headspace flushing, biogas recycling, chemical additives with the amount of revenue recovered from improved methane production.

2.4. Scope for VFA production

VFAs are the products from the initial acidogenic phase and mainly include acetic acid, propionic acid, butyric acid, and valeric acid, which are the precursors of methanogenesis (Morgan-Sagastume et al., 2011). They are identified as potential sources of fatty acid methyl esters (FAMES), fatty alcohols and medium length chain fatty acids through proven experimental results (Elain et al., 2016; Jung et al., 2016; Koutinas et al., 2014). During AD process, high level of VFA accumulation leads to the inhibition of methanogenesis and microbial stress (Fezzani and Ben Cheikh, 2010; Xu et al., 2014). Thus, recovering VFA works against the organic acid build up and supports the methanogenic activity (Huang et al., 2016; Jiang et al., 2013).

Currently developed AnMBR models for VFA production includes the two-stage assembly where VFA is produced at the initial hydrolytic stage (Wijekoon et al., 2011). As it is generated via hydrolysis process, the primary challenge is to separate the VFA from water through conventional or membrane distillation process (Jung et al., 2016). Generally, the VFA extraction process is largely affected by a number of factors such as fractionation efficiency of removed acids (Scoma et al., 2016), biomass washout with a sudden change in flow rate (Wijekoon et al., 2011), presence of impurities and high water content (Jung et al., 2016). Till now, ammonia stripping and electrodialysis have been developed for VFA extraction during anaerobic digestion (Huang et al., 2016; Scoma et al., 2016).

Wijekoon et al., (2011) characterized the change in VFA production from a two stage anaerobic membrane bioreactor via gas chromatography with different organic loading rates and temperatures. Results from the experiments concluded that an increase in VFA generation is attributed to the increase of organic loading rate in the initial hydrolytic stage. In this connection, AnMBR treating concentrated wastewater with high organic content

would be more favorable for stable VFA extraction compared to a feedstock with low carbohydrate content such as municipal wastewater. For example, it has been reported that VFAs recovered from dephenolized olive mill wastewater through the process of electro dialysis is economically feasible (Scoma et al., 2016). Although VFA recovery has economic potential to produce high end valued products, the separation and purification technologies are yet to be optimized specifically for different AnMBR arrangements. Thus, AnMBR configurations designed to maximize VFA production with a wide range of substrate composition would be a potential area of research in the future.

2.5. Scope for Hydrogen production

The production of VFA from the second and third stages of anaerobic digestion also includes the production of gaseous molecular hydrogen (biohydrogen) and carbon dioxide. The major pathways of biohydrogen production could be from acetic acid, butyric acid or via fermentation process (Hosseini and Wahid, 2016; Xia et al., 2016; Guwy et al., 2011). Under AD process, the protons accept the electrons to form biohydrogen and the methanogens consume the biohydrogen to produce methane. On the other hand, if the production of biohydrogen is maximized, its high partial pressure reduces the production of organic acids and alcohols (Adekunle and Okolie, 2015). In this connection, it is particularly challenging to maximize the production of biohydrogen and VFA/ methane in a single stage AnMBR.

For the multiple stage arrangements, the results have been attractive. Research models have included the concept of coupling a continuous hydrogen fermenter with a commercial membrane bioreactor (Bakonyi et al., 2015). The results achieved were 1.13 mol H₂/mol glucose yield and 0.24 mol H₂/L.d production rate under different HRTs (From 12 to 92 h). Compared to the different bioreactor assembly, the findings demonstrated that AnMBR

provides more robust and consistent operating possibilities, despite the potential threat of membrane fouling.

Recent experiments include several arrangements for anaerobic bioreactors like two-stage UASB reactor, anaerobic sequencing batch reactor, down-flow structured bed reactors that have been applied for hydrogen production (Intanoo et al., 2015; Intanoo et al., 2012). The two-stage anaerobic digestion model usually contains initial hydrolysis/acidogenesis and final acetogenesis/methanogenesis stages where temperature and pH values are adjusted separately considering the growth rate of the microorganisms in individual stages. For maximum hydrogen production from the initial stage, heat shock and load shock treatment are applied for the selective inhibition of the methanogens (Jariyaboon et al., 2015). Later effluent from the first stage is fed to the second stage of the reactor and favorable conditions (pH and temperature) are applied in the second stage for the optimum growth for the methanogens. Unfortunately, no AnMBR model has been designed yet to produce biohydrogen only, hence the advantages for biohydrogen production only is still not identified.

3. Economic Assessment

In spite of having great promises, the application of AnMBR is very limited compared to aerobic membrane bioreactor (AeMBR) in wastewater treatment or other waste disposal industries. The primary reason is attributed to the concern that the amount of energy recovered here cannot necessarily exceed the initial installation and high operational cost.

However, this limited economic feasibility may be a result of not considering the situation for maximizing intermediate AnMBR products. The following paragraphs include individual and comparative discussions about economic feasibility when AnMBRs with different

arrangements are designed to produce VFAs, biohydrogen and methane individually or simultaneously.

3.1. Assessment of methane Production

The current commercialization of AnMBR digestion focuses on maximum biogas production and its main constituent, methane. It is clear to which extent product of methane remains the major driver of the anaerobic digestion process. Firstly, compared to the other AD products methane has the advantage of limited downstream processing, the created biogas can directly be utilized for fuel with or without further purification, and for chemical intermediates. The second advantage is, production of methane involves low energy consumption, and the process uses all biodegradable organic matter and produces a high yield (Kleerebezem et al., 2015). Although Methane is considered as a suitable energy source with low cost, the production rate of methane varies with substrate composition. As a result, stable methane production rate has been a common problem for anaerobic digestion, because the feed with low organic content cannot provide sufficient organic carbons for methane production. Pretel et al. (2015) evaluated the design parameters for an submerged AnMBR under different solid retention time (13-41 days), organic loading rates (10-15 g/l MLSS) and operating temperatures (15 - 30 °C). In addition, the initial installation (sizing and construction of reactor, pumps and membrane) and operating cost (gas sparging, filtration and pump operating) of 100% biogas or total methane recovery were calculated against the product revenue from methane. According to the results, profit from total methane recovery had negative values represent net profit (ranging from -0.005 to -0.002 euro/m³) against the total cost range from 0.130 to 0.079 euro/m³. This indicated that the revenue earned from methane production could not exceed the initial installation and operating cost of an AnMBR.

3.2. Assessment for production of VFA

The large-scale production of VFA is governed by the chemical synthesis that includes process of methanol carbonylation and catalytical oxidation reaction between ethylene and carbon monoxide (Scoma et al., 2016). However, detailed cost analysis is not yet available to compare the economics between conventional carbonylation and anaerobic digestion processes. From anaerobic digestion process, the extraction of VFAs could be performed simultaneously with methane or aiming at complete recovery of VFAs only. Peces et al. (2016) investigated primary sludge pre-fermentation under semi-aerobic conditions. Their experiments demonstrated both VFA recovery ($43 \text{ g COD}_{\text{VFA}} \text{ kg}^{-1} \text{ VS}$) and improved methane recovery at both 20°C and 37°C operating conditions.

VFA produced from the initial hydrolysis stage of anaerobic digestion process is a source of reduced chemicals such as alkanes, aldehydes, alcohols and ketones (Huang et al., 2016; Morgan-Sagastume et al., 2011; Peces et al., 2016; Scoma et al., 2016).

Polyhydroxyalkanoate (PHA), a biopolymer used for biodegradable plastics production, could be produced more economically from VFA enriched photosynthetic mixed culture (PMC) rather than the current pure culture systems by commercial industries (Fradinho et al., 2014). A comparison between the revenue earned from methane and VFA generation was performed by Kleerebezem et al. (2015) based on a cardboard production facility producing $5000 \text{ m}^3/\text{day}$ wastewater in closed cycle. The results included a revenue of 3.6 k€ from total methane recovery compared to 20.2 k€ revenue from PHA produced in a single day.

However, their cost analysis did not consider the operational cost for methane or PHA production and also the cost involved in downstream processing for product recovery, but the significant economic room encourages more detailed research work on economic feasibility assessment when VFA is produced from AnMBR.

3.3. Assessment for the production of biohydrogen

The production of biohydrogen using the anaerobic process has been a great idea for overcoming the problems posed by carbon emissions (Intanoo et al., 2015; Jariyaboon et al., 2015). The current industrial hydrogen production involves coal, natural gas and oil as favorable raw materials but all these processes are energy intensive and require significant quantities of fossil fuel (Hosseini and Wahid, 2016). Biohydrogen production via anaerobic fermentation could reduce production costs which compromise the efficiency of the current industrial process; it is a renewable enterprise and may represent sustainable and efficient energy in the future (Jung et al., 2011; Xia et al., 2015). Biohydrogen production from municipal waste and wastewater has already proved its sustainability but has the current drawback of low hydrogen yield (Hosseini and Wahid, 2016). The large-scale application of biohydrogen production has been greatly compromised by safety and economic issues involved in hydrogen storage (Lowesmith et al., 2014; Mohammadshahi et al., 2016). The current hydrogen storage system suffers from technical issues that include the corrosion and embrittlement in common materials such as carbon steels (Rezende et al., 2015).

For maximum hydrogen production, recently developed models mostly include simultaneous production of biohydrogen and methane (Intanoo et al., 2015; Jariyaboon et al., 2015) from the two-stage UASB reactor. Results from these experiments have provided improved methane recovery with the produced biohydrogen. Hence the cost recovery from these two stage anaerobic process is higher compared to the conventional anaerobic process.

The cost of hydrogen as fuel still remains on the higher side and production of biohydrogen could be a cost effective option. Not only the simultaneous production with methane but also

the individual production could be a feasible option. No research data is yet available regarding the condition when biohydrogen is considered as the only product from the AnMBR. Although multiple stage arrangements has a drawback for additional cost of initial installation (Reactor and membrane installation) and process operation(membrane fouling, temperature, pH control), the cost recovered through the production of hydrogen could be compared with the additional amount for multiple stage assembly.

3.4. Cost comparison considering different product spectrum from AnMBR

High fluctuations of industrial toxicants, different sources of waste result unstable biogas production rate as different amount of organic compounds are available for methanogenesis. This could be the single major problem acting against the widespread industrial application of AnMBR. Studies have been conducted to breakdown the initial installation and operating costs involved in AnMBR treating wastewater from different sources (Lin et al., 2011; Pretel et. al., 2014). Table 2 provides a summary based on the results from both experiments and it clearly indicates that major portion of the operating cost is associated with high energy requirement when biogas is recycled into the system.

Table 2

The heavy burdens of AnMBR economy mainly include low flux, membrane fouling, high capital and operational costs. Over last few years there have been a significant development on the reduction of membrane acquisition or replacement costs because the costs for membrane modules have significantly decreased (Ozgun et al., 2013). Regardless the AnMBR arrangement, during methane production high amount of energy is always required for gas

scouring and this energy supplement requires up to 46.7% of total operational cost of AnMBR (Lin et al., 2011; Pretel et. al., 2014).

For maximum methane production, the production of VFA is controlled down to the level where the reduction of pH does not inhibit the methanogenic activity (Yuan and Zhu, 2016). Simultaneous VFA and methane production could be an option, but the complete inhibition of methanogenic activity could provide the opportunity to reduce the cost of installation, energy consumption and application of wider operating range in AnMBR operation (Kleerebezem et al., 2015).

Unlike VFA, research models have already been developed to produce biohydrogen from AnMBR (Bakonyi et al., 2015; Kim et al., 2011). For biohydrogen production, two stage anaerobic digestion process offers improved process stability through COD elimination in methanogenic stage, eliminates the limitation in organic loading rates and provides an option to treat sewage sludge, dairy wastewater, food waste and agro-industrial wastes (Guwy et al., 2011). In this connection, assessments are required to compare the low cost of operation and added biohydrogen production with the high initial installation cost for multiple stage arrangement.

Energy required for gas recycling, range of applicable organic load, pH and temperature control for methanogens, rate control for hydrolysis/ acidogenesis and unstable methane production are the key factors that stand on the way of the economic feasibility of currently established AnMBR models. The alternate approach to produce biohydrogen and/or VFA only could be a potential solution that can improve the economic feasibility of AnMBR. The technical feasibility achieved from different anaerobic models has been correlated in table

3.Itsummarizes the economic and technical challenges associated with different products spectrum and provides the potential research options based on the theories and limited available results.

Table 3

4. Environmental Impact

Although AnMBR does good work by treating the waste materials or wastewater, negative environmental impacts associated with the products and effluents does not make it the best option for anaerobic digestion process. The current major product methane and its combustion product carbon dioxide have been identified as major contributors in greenhouse gas emission.

4.1. Contribution to global carbon emissions

The world has clearly recognized the devastating effects of climate change and current political agendas do clearly focus on reducing CO₂ emissions from burning of fossil fuels (Cucchiella and D'Adamo, 2013). Many strategies have set out to develop renewable and clean energy sources to mitigate the problem of finite fossil fuel reserves and environmental problems associated with these fuels (Wei et al., 2013).

The carbon dioxide emission rate has been growing exponentially by the continual increase of the fossil fuel usage. Optimizing the process parameters in AnMBR for maximum methane production provides a sustainable option for bioenergy production. However, the development of this emerging technology would also contribute to the rising trend of global carbon dioxide emission. Besides contributing into the greenhouse gasses, there are other

environmental issues associated with the AnMBR products; the following paragraphs contain the effect of AnMBR products on the environment.

4.2. Environmental impact of different AnMBR products

Global warming, acidification, eutrophication, abiotic depletion and maritime aquatic ecotoxicity have been identified as the major environmental impacts from the products of AnMBR (Pretel et al., 2016). In a separate study, Pretel et al. (2013) evaluated the environmental impact of different products and effluents originating from submerged anaerobic MBR (SAnMBR). The assessments were based on three operating temperature conditions - ambient 20°C, 33°C and controlled 33°C. The results obtained from the study are summarized in table 4.

Table 4

The content of nitrogen and phosphorus in the digestate is not dependent to the anaerobic digestion process and their percentage mainly depends on the type of substrate that is being processed (Puchongkawarin et al., 2015). Negative environmental effects like eutrophication, aquatic eco-toxicity, acidification and human toxicity are directly attributed to the degradation rates of total COD, amount of total nitrogen, phosphorus and finally the production rate of methane (Pretel et al., 2013). Thus, tuning AnMBR parameters for improved nutrient recovery could be an option can partially reduce some negative effects but controlling the product spectrum could be an effective option to reduce environmental impacts caused by methane.

The impact category of GWP (Global Warming Potential) is associated with the amount of energy required for AnMBR operation. The model designed for methane production has already been identified as energy intensive for gas scouring and supplying heat energy to increase methane production (Lin et al., 2011; Pretel et. al., 2014). Both factors contribute to the impact category of GWP in AnMBR operation. Apart from the energy requirements, the produced raw biogas from AnMBR constitutes the major component of methane and CO₂.

There is no argument that methane and carbon dioxide directly contributes to the greenhouse gas emissions followed by the environmental GWP on the environment. Direct discharge of methane into the atmosphere is also possible by the fugitive emission from AnMBR. In addition, if not handled properly, dissolved methane could also be present in the AnMBR effluent. Low temperature operating conditions in AnMBR can create an effluent that contains more than 50% of methane (Pretel et al., 2016). Since the GWP of methane is approximately twenty-three times that of carbon dioxide, 5% emission could simply undermine and negate the positive impact of anaerobic digestion (Kleerebezem et al., 2015). To capture dissolved methane from bioreactor effluent, degassing membrane system has been a relatively new concept but the recovery system is yet to achieve the optimization. Impact categories like human toxicity, fresh water aquatic eco-toxicity, terrestrial eco-toxicity and marine aquatic eco-toxicity are directly affected by the presence of dissolved methane in the AnMBR effluent (Pretel et al., 2013).

Fatty acid methyl esters (FAMES) derived from VFAs can be used as a green solvent due to their low toxicity and high biodegradability (Jung et al., 2016). Another derived product, PHA, could be degraded by the microorganisms that secretes depolymerase enzymes to hydrolyse the bonds of ester polymers (Elain et al., 2016). Besides, recovery of VFA

diverts part of available organic carbons in the anaerobic digestion; it eventually reduces the methane production followed by the reduction of environmental impacts associated with greenhouse gas emission (Puchongkawarin et al., 2015). Therefore, anaerobic digestion process designed for maximum VFAs production could be applied in AnMBR design. Practical research work in this connection would contribute to eliminate the negative environmental impacts from AnMBR associated with methane production.

Production of biohydrogen is a sustainable solution against energy crisis and also offers the advantage of zero negative effect on the environment. As a fuel, hydrogen has a clean combustion product (H_2O) and high energy density by mass of 142 MJ/kg (Guwy et al., 2011). However, full scale application of biohydrogen production from anaerobic digestion process is still in the embryonic stage because of its high production costs and expensive storage system. Studies on the hydrogen storage system indicate that the current production process is not cost effective and not particularly friendly to the environment since it involves the consumption of a significant amount of fossil fuels (Kaini and Mondal, 2014; Lowesmith et al., 2014; Mohammadshahi et al., 2016; Rezende et al., 2015). In this connection, biohydrogen production could be the worthy alternative over methane where both the production and the consumption process offer minimum effect on the environment.

5. Impact on scientific society

5.1. Community perception

Recent publications have reported that the scientific community is increasingly interested in producing biofuels from biodegradable wastes (Ozgun et al., 2013; Smith et al., 2014). The scientific community engaged in bioresearch believes that a high level of viability and sustainability of biofuels has been achieved by employing these biodegradable wastes as

feedstock. Until now, the community's perception on biofuel generation is in the primary stage as the conventional energy production process still offers cost effectiveness over bioenergy. Considering the contribution in global power generation, only 1.8% of the power is from bioenergy (Sawin et al., 2015).

Although producing energy from anaerobic digestion process is in the early days, statistics show that the number of anaerobic waste management plant has been increasing sharply around the world. For examples, in 2014, the Anaerobic Digestion and Bioresource Association (ADBA) in London, UK reports a cumulative methane production rate of 19000 m³/h from 32 commissioned anaerobic plants, compared to a production rate of 2,000 m³/h from 6 new commissioned anaerobic processes in 2013 (More, 2015). In addition, in Europe, with a capacity of 8 million ton of organic waste, 244 anaerobic plants are operated to process about 25% organic wastes (Adekunle and Okolie, 2015).

There is no doubt, industrially AeMBR is still favored over the AnMBR despite the fact that AnMBR requires less energy compared to the aerobic system. The large scale introduction of AnMBRs has been limited for two main reasons. Firstly, people are more interested in the amount of bioenergy produced regardless of the type of waste material being treated. The low energy density compared to fossil fuels is a limitation for some applications and poses challenges to new business models (Richard, 2010).

Current research initiatives only provide an incomplete picture when comparing the drivers of different energy models. Most studies so far have selected single cases or regions to analyze specific situations. In this case, the promising results obtained from different anaerobic digestion models have not been implemented through design modification of existing

AnMBR arrangements. Research initiatives on the valorization of the intermediate products are still in its infancy and no large-scale industrial application yet has been occurred.

5.2. Adaptation of environment friendly products from AnMBR

For the scientific community, developing cost effective synthesis and storage system for hydrogen energy is the primary area of focus as industries have already started making preparations for the application of hydrogen energy. Among other renewable energy sources, hydrogen has already been identified as the main alternative of fossil fuels because of its ability to power fuel cells in zero-emission electric vehicles. Market introduction has just been made for the fuel cell electric vehicles by the car makers. Automobile companies are entering the pre-commercial phase by progressing from prototype vehicles to small-scale production (Ball and Weeda, 2016). By the year 2025, the United States alone aims to put 3.3 million zero-emission vehicles powered by hydrogen fuel cells. Until 2023, the state of California alone aims to invest \$20 million annually to reach a goal of 100 hydrogen filling stations throughout the state (O'Malley et al., 2015).

Despite the fact that hydrogen has a high potential as a renewable energy source, it has not yet been considered by the general consumers because of its requirement of high cost, lack of available skills and technical knowhow. Relatively expensive hydrogen production by electrolysis has garnered considerable attention because it offers more flexibility for large-scale integration of intermittent renewable energies. Production of hydrogen by the anaerobic digestion process has been proven technically feasible but lack of investment and operating costs (Ferrer et al., 2015; Pretel et al., 2014; Pretel et al., 2015) are prohibitive, suggesting high values relative to the conventional single stage AnMBR. Before large-scale application can commence, the process demands optimization and comparative economic feasibility assessment of the current technologies (Mei et al., 2016; Miranda et al., 2016).

In the existing wastewater treatment plants using anaerobic digestion, VFA has already been identified to aid the biological nutrient recovery process and increasing the methane production from the final stage of anaerobic digestion. Major challenge lies ahead to reduce the cost of biosynthesis process for PHA, as the production cost in oil-derived plastics is still favorable (Elain et al., 2016; Fradinho et al., 2014; Peces et al., 2016). No research has been performed yet to produce an integrated PHA production process from VFA by assessing the cost for process operation and downstream processing required for product recovery. There have been pilot-scale attempts to maximize VFA production in the anaerobic digestion (Huang et al., 2016; Ma (H.) et al., 2016; Xia et al., 2016; Yin et al., 2016) but the findings are yet to be implemented using different AnMBR arrangements.

The scientific community and some industries have already adapted methane as the final product from the AnMBR but currently it is no better than fossil fuels. Since methane has only been considered as the end valued product, the appetite of AnMBR has not been made for limited economic feasibility. Research developments to produce alternate products have showed promise, but only for fragmented pictures or specific substrate conditions. Most of the achievements involve anaerobic digestion with different bioreactors, only a limited number of experiments have been performed on AnMBRs. Compared to different AnMBR products, it is evident that the community's perception of VFA and hydrogen is yet to be ascertained. The employment of both products requires more research in terms of economic feasibility and large scale application. Before industrial application, it is required to develop generic research models of AnMBR where the product spectrum could be controlled by altering the operating conditions or bioreactor arrangements. The feedstock composition would be the challenging factor when concentration is given for a particular product.

6. Conclusion

Production of methane could provide the option for energy recovery from anaerobic process but it equally contains negative environmental impact and cost intensive operation.

Considering the long-term beneficial effects, intermediate products like biopolymers, medium chain fatty acids, bio hydrogen and other valued products could constitute a better alternative compared to what is being used currently. The technical feasibility and having minimal impact on the environment encourage the alternate process options for AnMBRs. The technical feasibility of an individual process demands an integrated analysis that could provide a better economic efficiency. This refers explicitly to producing VFAs and biohydrogen from AnMBRs.

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Figure captions

Figure 1 Schematic Diagram (a) Side stream (external) (b) submerged of AnMBR configurations

Figure 2 Major phases of anaerobic digestion

ACCEPTED MANUSCRIPT

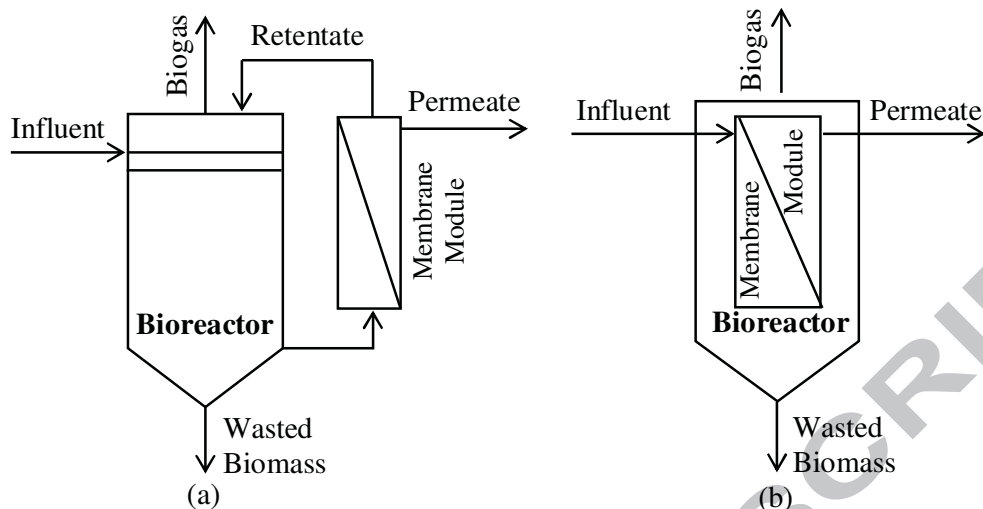


Figure 1

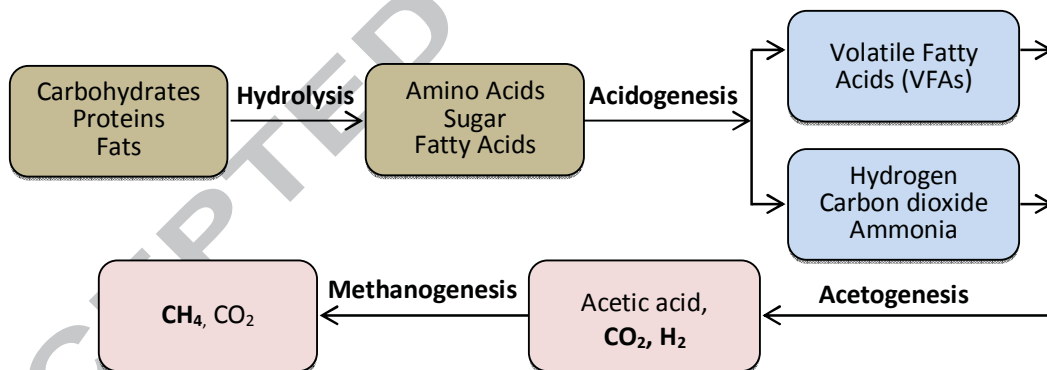


Figure 2

Table 1 Optimal operating conditions of AD process

Parameter	Operating condition	Positive and Negative effects	Recommendation
Temperature	Thermophilic	Rate advantage, high yield of methane. Acidification, low quality effluent, temperature sensitive, high energy requirement (Mao et al., 2015)	Thermophilic
	Mesophilic	More stable, higher richness in bacteria Less methane production, nutrient imbalance (Bowen et al., 2014)	hydrolysis/ acidogenesis and mesophilic methanogenesis
	Hyper-Thermophilic	Resilience in treating high concentrations of proteins, lipids. High energy requirement, More sensitive to temperature change (Lee (M.) et al., 2009)	
pH	6.5 – 8.2	High rate of Methanogenesis Low VFA production (Lee (D.H.) et al., 2009)	For two stage AD process, pH 5.5-6.5 could be applied to
	5.5 - 6.5	Maximum VFA production Inhibition of methanogenic bacteria (Kim et al., 2003)	hydrolysis and 7.0 for the methanogenesis (Mao et al., 2015)
C/N Ratio	25:1 – 30:1	Optimum overall biogas	-

		(Methane) production(Wu et al., 2010)	
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Table 2 Breakdown of total life cycle capital cost, operating cost and energy consumption in different AnMBR process (data adapted from Lin et al., 2011; Pretel et. al., 2014)

Submerged AnMBR treating 20000 m ³ volume municipal wastewater				AnMBR treating (3.2±0.7 m ³ /day) sulphate-rich urban wastewater	
Total Life cycle capital cost (%)		Operating Cost (%)		Energy consumption (%)	
Tank Installation	11.3	Gas Scouring Energy	46.7	Biogas recycling blower	73.5
Membranes	72.3	Pumping Energy	13.7	Sludge feeding pump	14.6
Screens	5.9	Sludge Disposal	7.2	Stirring power reactor	8.3
Gas Blower	5.5	Chemical Consumption	32.5	Permeate pump	1.8
Other Costs	5.0			Other Consumers	1.8

Table 3 Summary of the proposed AnMBR models for different product band from AnMBRs

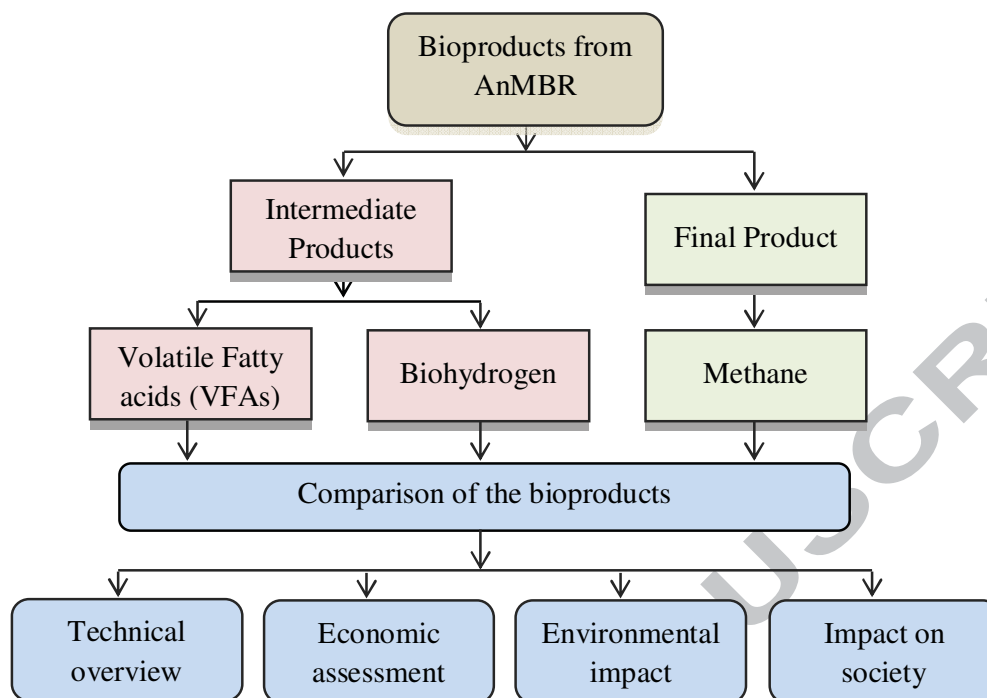
Production Band	AnMBR Model	Major Challenges	Recommendation
Biohydrogen, VFA and Methane	Multiple stage	High installation cost, high operating cost, process optimization	Economic feasibility could be assessed whether the cost recovery by producing hydrogen and VFA could exceed the installation cost.
VFA and methane	Single stage	Process optimization, reactor design	Feasibility study for multiple stage AnMBR
VFA	Single/ Multiple stage	Process optimization, utilization of all terminal stage products	A new AnMBR model with the inhibition of methanogenesis step (Kleerebezem et al., 2015) could be implemented through research
Biohydrogen and methane	Multiple stage	High installation cost, High operating cost (biogas recycling, control against membrane fouling)	Developed research models have proven the technical feasibility (Intanoo et al., 2014; Jariyaboon et al., 2015; Zhong et al., 2015). Economic feasibility could be assessed.

VFA and biohydrogen	Single/ Multiple	Process optimization, product spectrum control	The alternate approach (Kleerebezem et al., 2015) could be implemented by research
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Table 4 LCA results of submerged AnMBR. Method: CML 2 baseline 2000 V2.05/West Europe, 1995/Normalisation/Excluding infrastructure processes (modified from Pretel et al., 2013)

Impact Category	Ambient 20 °C	Ambient 33 °C	Controlled 33 °C (at ambient 20 °C)
	Total (X 10 ⁻¹⁴)		
Eutrophication	158.8726	159.1307	191.6357
Marine aquatic eco-toxicity	11.6750	10.9076	362.4733
Acidification	7.7487	6.6890	184.0135
Terrestrial eco-toxicity	7.4031	7.0542	31.7411
Fresh water aquatic eco-toxicity	70.7456	76.8873	80.7569
Abiotic depletion	3.2047	2.8501	576.6242
Global warming (GWP100)	2.5455	2.3352	227.7044
Human toxicity	69.7208	76.3144	95.9476
Photochemical oxidation	0.3407	0.3145	24.0949
Ozone layer depletion (ODP)	0.0061	0.0055	1.1397



Highlights

- Current AnMBRs mainly focuses on final bioproducts - methane.
- Technical feasibility shows the comparable value of intermediate AnMBR bioproducts.
- Alternate AnMBRs based VFA and biohydrogen production is considerable.
- VFA and biohydrogen production are a cost recovery option for AnMBR.
- Environmental impacts are associated with different AnMBR bioproducts.

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