Process simulation for biogas upgrading and biomethane recovery using biofilm-based reactors

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Abstract: Microbial biofilm matrices offer numerous benefits in bioprocessing and are crucial in various industrial and remediation processes. They facilitate electron exchange from solid surfaces when they interact with the environment. Emerging technologies such as biofilm-containing trickle bed reactors (TBR) and bioelectrochemical systems (BESs) for carbon dioxide (CO_2) utilization, mostly rely on microbial biofilm matrices. Metabolic modeling of biofilm-based reactors enables detailed analysis of CO_2 reduction within microorganisms, enhancing reactor efficiency. This study employed simulation models to analyze biomethane synthesis within TBR and BES systems. AQUASIM simulation tool was used for conducting the simulation. Parameters such as non-stoichiometric and stoichiometric ratios of substrates, hydraulic retention time (HRT), biofilm surface area, and applied voltage in BES were varied to evaluate methane (CH_4) production and microbial biomass growth in TBR and BES. Results demonstrated that 1 day HRT resulted in methanation process failure due to biomass development problem in both TBR and BES. The substrate ratio 1:4 of CO_2 to H_2 increased CH_4 production in the investigated reactors. In BES, in-situ CO_2 and proton (H^+) generation from oxidation reactions can increase CH_4 production. Whereas in TBR, external H_2 (hydrogen) should be supplied to consume higher amount of CO_2. The lag phase in TBR was shorter than that in BES because of the greater surface area in TBR. In BES, higher voltage increased the current generation because of development of more biomass on the cathode. The simulation underlines the influence of different variables on biofilm-based reactors, offering critical insights for experimental process design.

Keywords: Biofilms, Trickle bed reactor, Bioelectrochemical system, Methane, Carbon dioxide, and Hydrogen

1. INTRODUCTION

In recent decades, bioreactors have gained significant interest for biofuel production, and water and soil remediation due to several environmental advantages. Trickle bed reactors (TBR) which are designed for gas-liquid-solid interaction, can be applied in anaerobic condition for biomethane (CH_4) production (Germec et al., 2020). TBR offers high surface area from carrier materials that result higher mass transfer compared to conventional batch and continuous flow reactors (Orgill et al., 2013). Other types of advanced bioreactors are bioelectrochemical systems (BES) that take benefits from electrode-microbe interactions for wastewater treatment and biosynthesis of CH_4 or biochemicals (Pant et al., 2012). Recently, TBR and BES has been intensively applied for CH_4 production from CO_2 or organic waste from wastewater (Ayol et al., 2021).

Hydrogenotrophic methanogenesis in TBR takes place with ex-situ source of H_2. The process is less complicated, but the biggest limitation is the source of H_2 that should be ecofriendly and economical. In BES, H_2 or H^+ is generated in-situ at response of external voltage to convert CO_2 or organic carbon to CH_4. The reactor design is more complicated and requires durable electrodes to be applicable in large scale. Despite of complexity of such system, the benefit is that electrons, H^+ and CO_2 are released from anodic oxidation of organic compounds existing in wastewater. Then two mechanisms can dominate according to the external voltage. R.1 refers to direct electron transfer (DET) mechanism and R.2 is the indirect electron transfer when the cathodic reaction $2H^+ + 2e^- \rightarrow H_2$ takes place prior to CH_4 production (Eddy et al., 2014; Liu et al., 2019; Nelabhotla and Dinamarca, 2019). R.2 is the governing reaction for CH_4 production in TBR as well.

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad \text{(R.1)}$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \text{(R.2)}$$

During anaerobic digestion (AD), the organic matter is broken down by anaerobic microorganisms resulting in CH_4 evolution. However, it is not possible to digest the entire organic matter due to microbial limitations to degrade compounds such as lignocellulose mass and fibrous materials. This results in undigested biomass residues called sludge (Yan et al., 2022). It is not possible to use sludge as fertilizer if it is contaminated by toxic compounds. Therefore, the dried sludge can be utilized in thermal degradation process such as gasification to produce syngas that contains hydrogen (H_2), CO_2, CH_4, carbon monoxide (CO), oxygen (O_2), nitrogen (N_2) and other hydrocarbons. H_2, CO_2 and CO are feasible intermediates which can be fed to TBR or BES reactors for

production of biochemicals or CH_4 to upgrade biogas (Fericelli, 2011; Maj et al., 2017; Wang et al., 2023).
Other part of the AD effluent is called reject water that comes after mechanical pressing of sludge/ digestate, and contains low organic content, but still has a significant amount of biomass, nitrogen (N) and phosphorus (P) compounds (Fericelli, 2011; Meyer and Wilderer, 2004). The reject water can be used further as nutrient in TBR and BES for biofilm growth. Moreover, it can be treated at anode in BES reactor for organic matter removal (Verma et al., 2023). Autotrophic methanogens which can consume CO_2 along with H^+ or H_2 are dominant in the CH_4 production process. CO in syngas is also a useful energy source and electron donor/acceptor for methanogens through specific pathways (Lim et al., 2022).

Overall, bioprocesses are slow, and variable optimization by experimental studies can usually take from months to years. Process simulation can be a promising approach for process optimization without performing physical lab experiments. There are limited research reports which have done comparative investigation of different biofilm-based processes based on simulation. This work is a conceptual modelling and simulation study for comparison of TBR and BES reactors as different technologies in sludge and reject water management, for CH_4 recovery. In TBR, CO_2 to H_2 ratio from utilizing syngas is typically less than 1:4 which is the theoretical ratio of CO_2 to H_2 for complete CO_2 conversion to CH_4 (Wang et al. 2023; Eddy et al. 2014). Therefore, external H_2 source is needed for consumption of the entire supplied CO_2. In industrial perspective, if additional H_2 is supplied from fossil fuels, TBR process may not be ecofriendly. H_2 source will be sustainable if it is from green sources such as water electrolysis from renewable electricity (Chen et al., 2022). However, this may increase the cost of CH_4 production in terms of space, energy efficiency, and process complexity.

On the other hand, BES has the advantage of in-situ H_2 or H^+ evolution. Such reactors can be single chamber where anode and cathode are placed in the same compartment, or dual chamber where anode and cathode are separated by proton exchange membrane. In double chamber BES, higher voltage can be applied that leads to excessive H^+ generation. If higher voltage is applied in single chamber BES, it may result in O_2 evolution that inhibits methanogens. This is not problematic in dual chamber, since O_2 forms in the anode chamber, and only H^+ transfers to cathode. The source of H^+ in low voltage, mostly come from short carbon chain VFAs, but at high voltage, it can be organic nitrogen (NH_4^+), long chain carbohydrates, biomass, and water (Aryal et al., 2020; Batlle-Vilanova et al., 2019). The capacity of CO_2 conversion to CH_4 is evaluated to have a comparison, and for better understanding of BES and TBR in handling the CO_2 according to the availability of H_2.

2. METHODOLOGY

The concept of this comparative simulation study is shown in schematic diagrams in Figs. 1 and 2. Dried sludge from wastewater treatment plant and AD enters the gasification reactor. The reject water after centrifuge and dryer units will enter to TBR or BES for treatment via microbes. If the process is integrated with TBR (Fig. 1) CO_2 and H_2 from gasification enters to TBR for syngas upgrading into CH_4. In the alternative of integrating the process with BES reactor (Fig. 2), one input is H_2 and CO_2 from gasification. In addition, excess CO_2 and H^+ will be available from anodic oxidation of organic compounds in the reject water.

The amount of organic carbon and biomass in the dry sludge was calculated based on the ADM1 Batstone model (Batstone et al., 2002). The model is based on a 28 m^3 continuous stirred tank reactor with around 7 days HRT. The calculated biomass in AD effluent from the Batstone model was used to calculate the gaseous inputs into TBR and BES. In this stage, only H_2 and CO_2 from gasification was used for biomethane production in TBR and BES. The reject water which contained biomass, was used for biofilm formation on the bed of the TBR, and on the electrodes in BES.

AQUASIM (version 2.1) is used as the simulation software which comes with a one-dimensional multi-substrate and multispecies biofilm model. One-dimensional spatial profiles of the microbial species and substrates within the biofilm provides opportunity to forecast real conditions through simulation. Also, it is possible to predict the changes in substrate concentrations, microbial species, and biofilm thickness over time (Reichert, 1998; Wanner and Morgenroth, 2004).

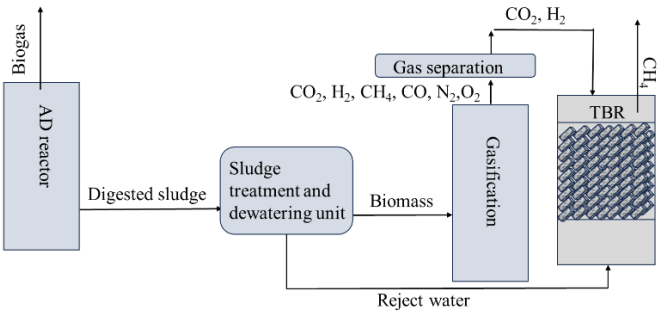

Fig. 1. Schematic diagram of the downstream biogas recovery process with alternative1: trickle bed reactor (TBR) unit. The treated sludge from AD flows to gasification unit. CO_2 and H_2 from syngas are applied for simulation of the TBR. Reject water enters the TBR for biofilm formation.

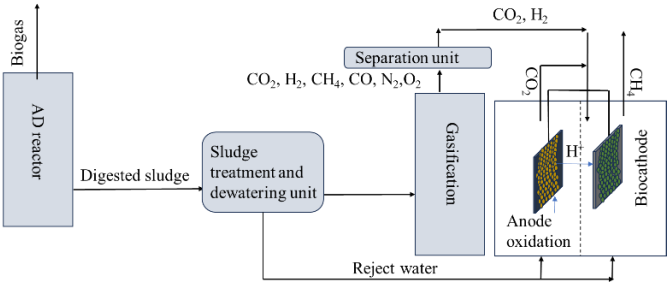

Fig. 2. Dual chamber BES reactor with proton exchange membrane. In case of BES, CO_2 and H^+ can be produced from oxidation of organic matter and water at anode. CO_2 flows out and enters the cathode. H^+ transfers to cathode through the membrane.

2.1 Model assumptions

- The reactors are operated at atmospheric pressure and pH 7.
- In both reactors, the diffusion is considered only on biofilm.

- CO_2 is the only carbon source for cathode which is soluble and in equilibrium with HCO_3^-.
- All the active biomass is attached. The detached biofilm does not interact with the biofilm reactions.
- Initial biomass fraction is equal for all species.
- In TBR, two types of methanogens grow on the biofilm that grow on CO_2 and H_2 with different yields.
- In BES, two types of methanogens grow on biofilm. One can directly consume CO_2 and H_2. The other one consumes CO_2 and H^+ via DET mechanism.
- In BES, a cathodic approach is followed, and only cathodic biofilm is involved in simulation of CH_4 production.
- Limitation of the process is the gaseous stream which can be enhanced by continuous flow and gas flow rate. The solubility of H_2 and CO_2 are not equal in atmospheric pressure. Diffusion coefficients can reflect these limitations in the biofilm.
- Every species has the same initial biomass proportion. The yields are assumed as close as possible for the methanogens in TBR and BES.
- Due to operating conditions, the detachment velocity in the simulation as described in Reichert (1998) is taken to be a measure of bacterial decay (K_d) and biofilm loss.

2.2 Simulation approach, inputs, and parameters

Two biofilm-based reactors with continuous flow of gases and biomass are stablished for the simulation. The flow gases are assumed to come from a gasification reactor which gasify around 1040 mol.m^{-3} of organic biomass. The syngas composition from gasification depends on various operating conditions such as temperature, pressure, feedstock and other factors. In this work, according to reported values for sewage sludge, the gasification reactor product is assumed to contain 20% CH_4, 15% CO_2, 20% H_2, 15% CO, 25% N_2, and 5% trace elements (Wang et al., 2023). If the gasification input is 1040 mol.m^{-3} of dry sludge with biomass structure formula of $CH_{1.8}O_{0.5}N_{0.2}$ (Heijnen and Kleerebezem, 1999), 312 mol CO_2 and 416 mol H_2 is obtained according to these considerations. This is assumed as the non-stoichiometric ratio of CO_2 to H_2 flowing into the TBR, and into the cathode chamber of BES.

Calculation of the concentration of excess CO_2 and H^+ in BES was done based on the oxidation half-reactions of organic compounds such as volatile fatty acids (VFAs), from the effluent of ADM1 model. Half-cell voltage inputs below -0.8 V vs SHE, leads to oxidation of organic matter, while it is often not enough for water oxidation. Therefore, the amount of generated H^+ is limited mostly by the organic matter such as short chain VFAs. Low voltage may not provide enough H^+ for reduction of entire CO_2 that flows to the cathode. Thus, higher voltage can be applied for providing more H^+ from oxidation of long carbon chain organic matter and water splitting.

Tab.1 gives the non-stoichiometric and stoichiometric ratios of CO_2, H_2 and H^+ to the TBR and BES reactor. In TBR reactor, H_2 was considered from external source. For BES, -0.8 and -1.5 V vs SHE was assumed which the lower voltage provides limited H^+, and the higher voltage can generate enough H^+ for the complete reduction of CO_2 input.

Table 1. CO_2, H_2 and H^+ inputs for TBR and BES

CO_2 to H_2 ratio from gasifier (mol.m^{-3})	CO_2 to H^+ from oxidation of organics at -0.8 V vs SHE (mol.m^{-3})	Excess H_2 for TBR, and H^+ generated from organics and water oxidation at -1.5 V vs SHE (mol.m^{-3})
CO_2: 312 H_2: 416	CO_2: 42 H^+: 246	H_2: 832 H^+: 1754

Some of the parameters are contemplated equal for both TBR and BES as shown in Tab. 2. The inlet flow rate (Q_{in}), initial biomass concentration, the initial biofilm thickness, and the reactor volume are equal in both reactors. It should be noted that the volume of cathode in BES is equal to the total volume of TBR. Since the inputs are of high quantity, lower than a specific volume is not possible to apply. The volume of dual chamber BES was two times greater than TBR. The typical TBR bed area to reactor volume ratio is assumed between 100-1000 m^2.m^{-3} (Manjrekar and Mills, 2022). The cathode size to reactor volume in BES is assumed between 10-100 m^2.m^{-3} (Rabaey and Verstraete, 2005). So, the surface area is adjusted according to these general ratios.

For the autotrophic microbes in TBR, the biomass yield is 0.05-0.3 (Eddy et al., 2014; Thauer et al., 2008). Thus, the yield was considered in the middle range between 0.1 and 0.15. For the BES reactor, the yield can be lower, because the imposed electricity can enhance microbial growth. So, yield of 0.083 (Ahmadi and Aryal, 2024) was taken for electroactive microbes via DET which consume H^+ and CO_2, and 0.1 for H_2 and CO_2 methanogens. Since the biomass yield has a big impact on CO_2 reduction, both reactors must have close biomass yield to be comparable. The yields which fitted the simulation, were obtained by trial and error.

2.3 Model expressions

In TBR simulation, multiplicative Monod equation can be used for calculation of CH_4 production and methanogenic biomass growth ($\frac{d[X_{CH_4}]}{dt}$). Here, H_2 is the electron donor to the microbes, and CO_2 is the only electron acceptor as shown in (1).

$$\frac{d[X_{CH_4}]}{dt} = X_{CH_4} \cdot \left(\mu_{X_{CH_4}}^{max} \cdot \frac{S_{CO_2}}{K_{CO_2}+S_{CO_2}} \cdot \frac{S_{H_2}}{K_{H_2}+S_{H_2}} - k_{d,CH_4} \right) \quad (1)$$

Where X_{CH_4} refers to methanogenic biomass content, $\mu_{X_{CH_4}}^{max}$ is the maximum growth rate of methanogens, S_{CO_2} is the molar concentration of CO_2, K_{CO_2} is the half-saturation constant of CO_2, S_{H_2} is the molar concentration of H_2, K_{H_2} is the half-saturation constant of H_2, and k_{d,CH_4} is the decay rate of methanogens. The values of each parameter with units are given in Tab. 2.

In BES simulation, methanogens can consume the in-situ generated H^+ via DET. So, the electron acceptor in Monod expression is H^+ together with CO_2. Both components are limiting factors for CH_4 production. Cathode performs as the

electron donor. The Nernst term in (2) presents the role of electron donor in electroactive CH_4 production. In theory, cathodic reactions are the opposite of anode reactions in terms of the signs.

Table 2. Parameters required for simulation of TBR and BES

Parameter, Unit	Value	Ref
Diffusivity of CH_4, $m^2 \cdot d^{-1}$	$1.296 \cdot 10^{-4}$	(Ahmadi and Dinamarca, 2022)
Diffusivity of CO_2, $m^2 \cdot d^{-1}$	$1.658 \cdot 10^{-4}$	(Ahmadi and Dinamarca, 2022)
Diffusivity of H_2, $m^2 \cdot d^{-1}$	$4.43 \cdot 10^{-4}$	(Ahmadi and Dinamarca, 2022)
Diffusivity of H^+, $m^2 \cdot d^{-1}$	$8.04 \cdot 10^{-4}$	(Ahmadi and Dinamarca, 2022)
Diffusivity of biomass, $m^2 \cdot d^{-1}$	$1 \cdot 10^{-7}$	(Ahmadi and Dinamarca, 2022)
Biomass density, $mol \cdot m^{-3}$	222	(Ahmadi and Dinamarca, 2022)
Half-saturation constant of CO_2, $mol \cdot m^{-3}$	1	(Eddy et al., 2014)
Half-saturation constant of H_2, $mol \cdot m^{-3}$	0.02	(Eddy et al., 2014)
Half-saturation constant of H^+, $mol \cdot m^{-3}$	$1 \cdot 10^{-4}$	(Eddy et al., 2014)
Max growth rate of methanogens_1 in TBR, d^{-1}	1.15	Assumed*
Max growth rate of methanogens_2 in TBR, d^{-1}	1.24	Assumed*
Max growth rate of methanogens_1 in BES, d^{-1}	1.32	Assumed*
Max growth rate of methanogens_2 in BES, d^{-1}	1.15	Assumed*
Yield of methanogens_1 in TBR	0.15	Assumed*
Yield of methanogens_2 in TBR	0.12	Assumed*
Yield of methanogens_1 in BES	0.083	Assumed*
Yield of methanogens_2 in BES	0.1	Assumed*
Boundary layer resistance, m	$1 \cdot 10^{-4}$	(Ahmadi and Dinamarca, 2022)
Initial biofilm thickness, m	$1 \cdot 10^{-9}$	(Ahmadi and Dinamarca, 2022)
Half-maximum growth voltage, V	-0.4	Assumed*
Applied potential on cathode, V	-0.8, -1.5	Assumed*
Cell synthesis coefficient	0.54, 0.4	(Eddy et al., 2014; Ahmadi and Aryal, 2024)
Cathode compartment volume of the BES, m^3	4	Assumed
TBR reactor volume, m^3	4	Assumed
Cathodic biofilm surface area, m^2	400, 2000, 4000	Assumed
Trickle bed surface area, m^2	40, 200, 400	Assumed

Therefore, the Nernst term which is originally obtained from anodic reactions and anode respiring bacteria (ARB), will be opposite sign in the cathodic approach (Ahmadi and Dinamarca, 2022; Eddy et al., 2014; Rittmann and McCarty, 2020; Torres et al., 2008). The biomass growth rate of electroactive microbes ($\frac{d[X_{CH_4,el}]}{dt}$) can be calculated via (2).

$$\frac{d[X_{CH_4,el}]}{dt} = X_{CH_4} \cdot \left(\mu_{X_{CH_4}}^{max} \cdot \frac{1}{1+exp\left[(E_{app}-E_{KA})\frac{F}{RT}\right]} \cdot \frac{S_{CO_2}}{K_{CO_2}+S_{CO_2}} \cdot \frac{S_{H^+}}{K_{H^+}+S_{H^+}} - k_{d,CH_4} \right) \quad (2)$$

Where E_{app} is the cathodic voltage, F is the Faraday constant (96485.3 C. mol^{-1}), R is the gas constant (8.314 J. mol^{-1}. K^{-1}), T is the temperature (K), S_{H^+} is the molar concentration of H^+, K_{H^+} is the half-saturation concentration of H^+.

In the Nernst term in (2), the term E_{KA} is the voltage when the growth rate of microbes is half of the maximum growth rate. For cathodic microbes, this value falls in the reductive voltage region between the open circuit voltage (OCV) of cathode, and the optimum voltage of biocathode. Various work reported that higher CH_4 production takes place when the voltage is -0.8 and higher (Tremblay et al., 2019). This is due to H^+ evolution from heavy chain organics, inorganic matter, and water oxidation. Assuming cathodic voltage -0.8 V and OCV of the cathode is -0.25, E_{KA} can fall between -0.25 and -0.8 V. In this work, E_{KA} was taken as -0.4 V vs SHE (Torres et al., 2008).

The calculated Nernst term (Fig. 3) shows that when E_{app} is equal to E_{KA}, the Nernst term becomes equal to 0.5. So, the growth rate is half of its maximum. The approach is according to the kinetic study carried on by Kato Marcus et al., (2007). At E_{app} = -0.8 V, the Nernst term becomes equal to 1, giving the maximum growth rate. From -0.8 to -1.5 V, the Nernst term stays equal to 1. This means the maximum growth rate will be dependent on higher H^+ evolution. In dual chamber BES reactors, -1.5 V vs SHE results in massive H^+ generation which can be beneficial for higher CH_4 production in the cathode chamber.

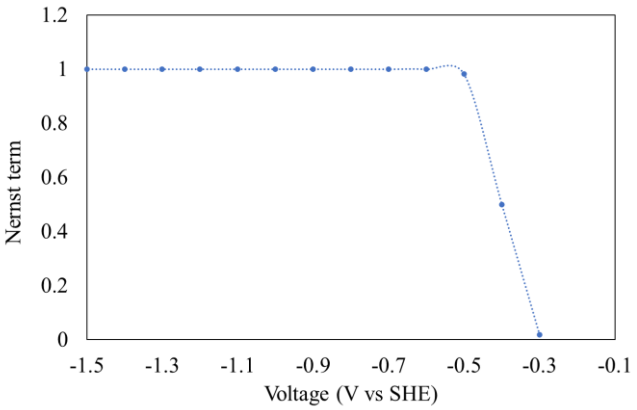

Fig. 3. The resulted values for Nernst term ($\frac{1}{1+exp\left[(E_{app}-E_{KA})\frac{F}{RT}\right]}$) at reductive applied voltage when E_{KA}= -0.4 V.

CH_4 production ($\frac{d[S_{CH_4}]}{dt}$) in both TBR and BES was calculated according to (3).

$$\frac{d[S_{CH_4}]}{dt} = \left(\frac{d[X_{CH_4}]}{dt}\right) \Big/ Y_{CH_4} \quad (3)$$

Where Y_{CH_4} refers to metahnogenic biomass yeild based on CO_2 and H_2 or H^+ consumption.

Change in current density, j ($\frac{dj}{dt}$, $A \cdot m^{-2}$) over time correlates to electroactive biomass concentration ($\frac{d[X]}{dt}$) and the biofilm thickness (L_f) which can be calculated by (4) (Torres et al., 2008).

$$\frac{dj}{dt} = \frac{d[X]}{dt} \cdot \gamma \cdot L_f \cdot (f_s^0 - 1) \quad (4)$$

Where γ is 8 which is the number of electrons required for CH_4 generation. The term f_s^0 is the fraction of mol substrate per mol electron equivalent used for cell synthesis. At high voltage, the cell synthesis yield becomes lower. The relationship between f_s^0 and voltage is assessed in another work considering the thermodynamics of the electrochemical reactions (Ahmadi and Aryal, 2024). Moreover, higher voltage increases the current density to the cathode (Aryal et al., 2016; Tremblay et al., 2019). The share of the current density that is consumed for electroactive biofilm growth can be obtained from (4).

3. RESULTS AND DISCUSSIONS

For TBR with non-stoichiometric inputs of 1:1.33 CO_2 to H_2 (Fig. 4), the plots are grouped for 3 surface areas with 3 different HRTs. The HRT has a bigger impact than the surface area according to the chosen parameters. The simulation shows that CH_4 production starts with a longer lag phase with 1 day HRT, then a steep methane production happens, but it ends with reactor failure that can be due to the detachment velocity. The corresponding lines for 1 day HRT are those with the highest methane production. Nevertheless, the process could not continue for 50 days, and collapses after 43 days. 4000 m^2 surface area helps reducing the startup time of CH_4 production. Higher surface area can be a better choice when handing higher H_2 inputs.

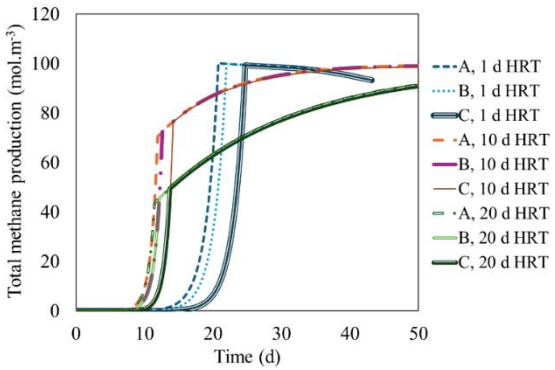

Fig. 4. Methane production in TBR with non-stoichiometric CO_2 to H_2 input. A: 4000 m^2, B: 2000 m^2, C: 400 m^2.

Moreover, 10 days HRT has the shortest startup time, even shorter than 20 days HRT. Also, 10 days HRT leads to higher CH_4 production compared to 20 days HRT. So, 20 days HRT is not efficient, and 1 day HRT is too short for the process. Therefore, to avoid process failure, and for high CO_2 conversion, 10 days HRT with 4000 m^2 surface rea (1000 $m^2.m^{-3}$) was taken as optimum design parameters for TBR with the defined process condition for further evaluation.

For non-stoichiometric conditions in BES (Fig. 5), the oxidation of organics at -0.8 V vs SHE, provides H^+ for the cathode which leads to higher CH_4 production compared to TBR. In BES as well as in TBR, 1 day HRT leads to process failure. 10 days HRT in this reactor is better for the process with a reasonably short lag phase of 9 days. Also, the corresponding CH_4 production indicates that all the H_2 and H^+ available for cathode is consumed for CO_2 reduction. The 400 m^2 surface area (100 $m^2.m^{-3}$) is advantageous because of a faster startup time which can be reduced to 7 days. Thus, 10 days HRT and 400 m^2 surface area can be taken for cathode for further assessment of stoichiometric inputs.

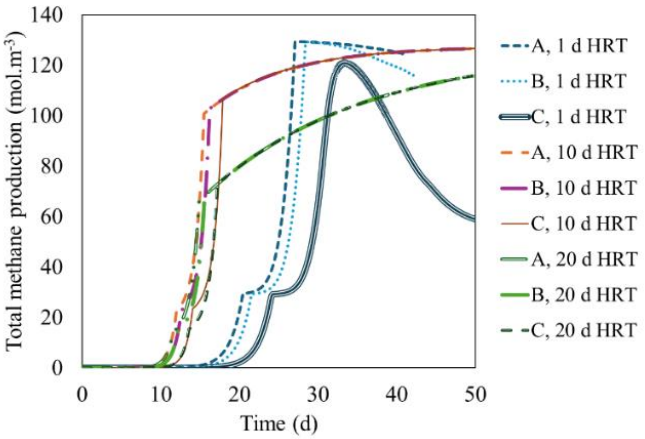

Fig. 5. Methene production in BES with non-stoichiometric CO_2 to H_2 or H^+ input. A: 400 m^2, B: 200 m^2, C: 40 m^2.

Nevertheless, to point out the reason of process deficiency in 1 day HRT for both TBR and BES, Figure 6 illustrates the biomass growth profiles in 1, 10, and 20 days HRT. As depicted in Fig. 6, in 1 day HRT, the biomass growth happens after 10 days with a fast slope, but a sharp decrement in biomass concentration occurs after 15 days in TBR, and after 28 days in BES. This means that failure in CH_4 production is relevant to biomass growth profile in 1 day HRT in both reactors. A possible biomass washout due to fast flow rate can be the reason for the loss of CH_4 production in TBR and BES. Moreover, washout happens earlier in TBR compared to BES reactor. Therefore, 10 and 20 days HRT gives better stability in BES and TBR. In practical experiments also, washout due to fast HRT is reported to cause production failure (He et al., 2024).

The biomass growth for both reactors in 10 days HRT is stable, and results in higher CH_4 formation (Figs. 4 and 5). The biomass growth profile peaks at day 9 in TBR, and reaches the highest at day 14 in BES. In 10 days HRT, the amount of biomass on the biofilm is higher than that in 20 days HRT, which results in higher CH_4 production.

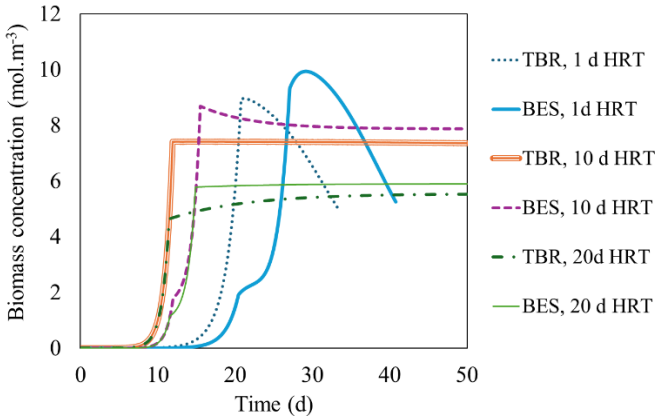

Fig. 6. Biomass concentration in TBR reactor with 4000 m^2 biofilm surface area, and in BES reactor with 400 m^2 biofilm surface area in non-stoichiometric condition at 1, 10, and 20 days HRT.

For evaluating TBR and BES in CO_2 reduction with stoichiometric input values, Figure 7 shows the results for 10 days HRT with 4000 m^2 biofilm area in TBR, and with 400 m^2 biofilm area in BES reactor. In Fig. 7, CH_4 production starts faster in TBR than that in BES. The production starts at day 8 in TBR, and at day 11 in BES reactor. Nevertheless, the amount of CH_4 which can be obtained by BES is higher than that in TBR. One reason is the surplus CO_2 which is generated from the oxidation of organic matter in BES. The other reason is the lower biomass yield in BES. In BES, as explained earlier, the biomass yield will be thermodynamically lower because the external electrical energy assists the cathodic biofilm to grow. So that, lower amount of CO_2 is consumed for cell synthesis. On the other hand, since the biomass yield and the maximum growth rate of microbes are considered close values, the biomass concentration reaches 22.88 $mol.m^{-3}$ in TBR, and 19.3 $mol.m^{-3}$ in BES. With stoichiometric H_2 input, 299 $mol.m^{-3}$ CH_4 will be produced, and the rest of CO_2 will be consumed for cell synthesis. In BES, 340.5 $mol.m^{-3}$ CH_4 will be produced, and the remaining CO_2 is consumed for cell synthesis. As it is obvious, in the BES reactor, H^+ is responsible for utilizing a bigger share of the CO_2 inlet. So, CH_4 that is generated from the electroactive methanogens is higher than the methanogens which consume H_2 for CO_2 reduction to CH_4.

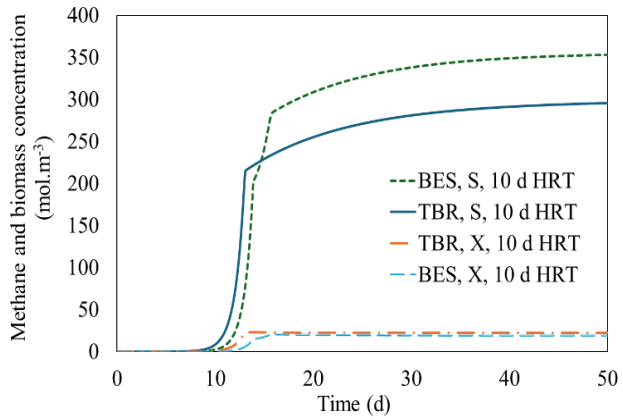

Fig. 7. CH_4 production and biomass concentration in TBR and BES reactor for stoichiometric values in 10 days HRT.

The current density was calculated using the electroactive biomass concentration together with the biofilm thickness which was obtained from the simulation. In the dual chamber BES, the generated H^+ at low and high voltage, is the result of current density and electron flow from anode to cathode. The amount of current density which correlates to electricity consumption for biomass growth can be calculated over time. However, at lower reductive voltage, lower biomass can aggregate on biofilm that corresponds to less CH_4 formation. Figure 8 shows that the reductive voltage for organic matter oxidation corresponds to -0.03 $mA.m^{-2}$ current density at -0.8 V vs SHE. Nevertheless, CO_2 reduction is low with respect to low H^+ generation. To generate higher H^+ to consume more CO_2, -1.3 $mA.m^{-2}$ current density is obtained. That means the amount of biomass which grows on biocathode, requires higher current density for complete CO_2 reduction. In a double chamber reactor, higher voltage results in higher H^+ generation (Pisciotta et al., 2012).

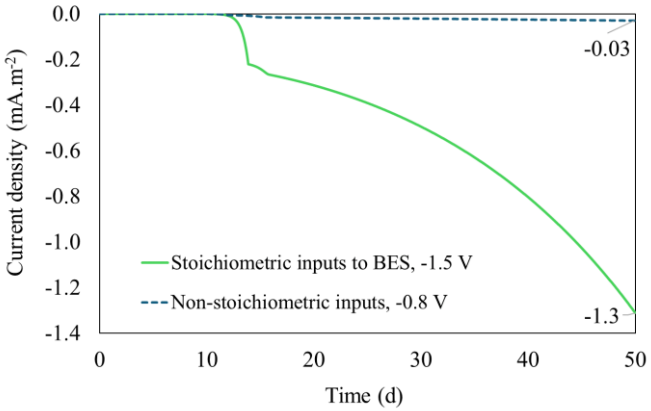

Fig. 8. Current density of the BES reactor at -0.8 and -1.5 V vs SHE corresponding to the current generation for non-stoichiometric and stoichiometric H^+ generation in the reactor.

4. CONCLUSIONS

This work carried on a preliminary study of the concept of TBR and BES reactors integrated with an AD reactor for downstream sludge treatment using gasifier and reject water treatment. The simulation showed that 4000 m^2 surface area for TBR and 400 m^2 cathode surface area for BES is beneficial for reducing the starting time of CH_4 production. 1 day HRT leads to operation failure. Therefore, in the defined operating conditions in this simulation work, in both processes, 10 days HRT led to stable and optimum CH_4 production. TBR is more straightforward than BES, however, greater amount of CH_4 can be achieved in BES reactor due to excess CO_2 and H^+ from BES process. The complexities of TBR are the source of excess H_2 that should be provided from green sources. Therefore, economical aspects of in-situ and ex-situ H_2 production should be studied further. Overall, both processes seem to be promising in valorizing CO_2 to CH_4. Moreover, CO is an electron donor source. So, in the next step of the study, CO will be studied together with CO_2 and H_2 in the biofilm processes.

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