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Short Communication

Kinetic study of biohydrogen production by anaerobic fermentation in a modified UASB-FF reactor

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ABSTRACT

Fermentative hydrogen production is a common anoxic process where the bacteria degrade organic matters to produce the required electron in the anaerobic reaction. Dark fermentation in the acidogenic phase utilizing obligated and facultative anaerobes leads to hydrogen (H_2) production. This method usually achieves a much higher H_2 production rate than other biological processes. The kinetic evaluation of biological hydrogen production using palm oil mill effluent as substrate was done in a modified up-flow anaerobic sludge blanket –fixed film (UASB-FF) reactor. In this study, the two factors of feed flow (Q_F) (1.7-10.2 l/d) and up-flow velocity (V_{up}) (0.5-3.0 m/h) were chosen as the independent variables to investigate the bioreactor performance. The maximum specific growth rate (μ_{max}) of hydrogenesis bacteria grown on POME as substrate was obtained at 0.313 d^{-1} (38 °C). The half-velocity constant (Ks) was 9.04 g/L when POME concentration was 15.0 g/L. In this study, the kinetic parameters of Y, K_d, and k calculated were 0.1 g/g, 0.0043 d^{-1}, and 3.13 g COD/g VSS.d, respectively.

1. Introduction

Emissions emanating from the combustion of fossil fuels leads to some adverse environmental impacts. These emissions, that contain COx, NOx, and SOx, are claimed to contribute to global warming, ozone layer depletion, and acidic deposition. Hydrogen (H_2) is a promising fuel due to its high energy yield (122kJ/g) which is 2.4, 2.8 and 4 times higher than energy yields of methane, gasoline and coal, respectively (Zadariana et al. 2009; Mohammadi et al. 2014).

Recently, significant attention is directed towards the use of H_2 as an alternative and eco-friendly energy source throughout the world. Different hydrogen production methods have been reported, for example, fossil fuel reforming (Hameed and Gondal 2005), biological processes of biomass (Chang et al., 2002), and electrolysis of water (Zhou et al., 2004). H_2 production through the biological process is known as a low energy intensive method, where processes can be operated at ambient temperature and pressure (Leite et al. 2008).

Amongst biological methods, fermentative hydrogen production has become more favorable due to some outstanding advantages such as high hydrogen production rate (HPR), low energy requirement, relatively easy operation, and high sustainability (Wu and Chang, 2007; Zhang et al., 2008). Fermentative hydrogen production is a common anoxic process where the bacteria degrade organic matters to produce the required electron in the anaerobic reaction. This technique provides a specific condition under which acidogens (hydrogen producing bacteria) and methanogens (hydrogen consuming bacteria) exhibit an imbalance in their activities resulting in accumulation of hydrogen (Leite et al. 2008).

Dark fermentation in the acidogenic phase utilizing obligate and facultative anaerobes leads to H_2 production. This method usually achieves a much higher H_2 production rate than other biological processes (Das and Veziroglu 2001; Levin et al. 2004; Wu and Chang 2007). In this study, application of a modified UASB-FF reactor to produce H_2 from palm oil mill effluent (POME) was investigated. The main objective of this research was kinetic study of biohydrogen production from POME in the UASB-FF bioreactor.

2. Materials and methods

2.1. Experimental set-up

The Lab-scale UASB-FF bioreactor (total volume 3.5 L, working volume 2.55 L, liquid height 80 cm) was fabricated and performed in this research (Mohammadi et al. 2014). There are more details about the bioreactor and experimental set-up in the previous published article (Mohammadi et al. 2014). The temperature of the bioreactor throughout of experiment was maintained at 38 °C by hot water circulation and pH was 5.5.

In this study the two factors i.e. feed flow (Q_F) and up-flow velocity (V_{up}) were chosen as the independent variables for the purpose of modeling. The range of Q_F and V_{up} investigated for biological hydrogen production from POME were 1.7-10.2 l/d and 0.5-3.0 m/h, respectively. In this study, the influent COD concentration of pre-settled POME was maintained at 15000 mg/l in all experiments. Therefore, Q_F was determined to be in the range of 1.7 to 10.2 l/d (corresponding to HRT of 36 to 6 h) in order to find the optimum conditions for increasing the effluent quality and process stability. This would cover an OLR range of 10 to 60 g COD/l.d. Selection of the range of the OLR studied was based on the results obtained from previous studies by other researchers.

2.2. Analytical techniques

The parameters viz. BOD, COD, TSS, VSS, alkalinity, total Kjeldahl nitrogen (TKN), oil and grease, and pH were an analyzed using procedures outlined in the APHA Standard Methods (APHA, 2003). The biogas composition was determined using a gas chromatograph (Perkin Elmer, Auto system GC), equipped with thermal conductivity detector (TCD) and data acquisition system namely Total Chrom ®

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software. H_2 content was also analyzed by GC-TCD fitted with a 1.5 m stainless steel column (SS350A) packed with a molecular sieve (80/100 mesh). The temperature of the injection port, oven and detector were 80, 200, and 200 °C, respectively. Argon was used as a carrier gas at a flow rate of 30 mL/min.

3. Results and discussion

The fermentation of organic substrate is a relatively complex process, by which the organic compounds are converted to liquid organics and biogas (i.e. H_2 and CO_2). The hydrolysis conversion rate and the soluble substrate utilization rate for fermentation are two important rate-limiting steps in anaerobic biohydrogen production processes. POME includes some volatile acids, hydrolyzable substrate and simple compounds that are used for metabolism by the fermentative bacteria. Therefore, the fermentative hydrogen production process from POME must be considered in the kinetic terms. The fermentative process is commonly modeled as a first order reaction with respect to substrate concentration (Droste 1997). In fermentation processes the main part of hydrolyzable substrate are hydrolyzed in specified HRT and subsequently utilized by acidogenesis and hydrogenesis bacteria. The equation (1) below is used in the substrate mass balances:

$$\frac{ds}{dt} = r_{su} = -\frac{k.S.X}{K_s + S} \quad (1)$$

where r_{su} is rate of substrate concentration change due to utilization (mg/l.d), k is maximum specific substrate utilization rate (mg COD/mg VSS.d), X is biomass concentration (mg VSS/l), S is substrate concentration (mg COD/l), and Ks is half-velocity substrate constant (mg/l).

The Monod equation is an appropriate model to describe and calculate the microbial growth parameters of fermentative anaerobic reactions.

$$\frac{1}{\mu} = \frac{K_s}{\mu_{max}} * \frac{1}{S} + \frac{1}{\mu_{max}} \quad (2)$$

The kinetic parameters were calculated according to equation (2) and the Line weaver-Burk plot (Fig. (1)). According to Fig. 1, slope equals to $\frac{K_s}{\mu_{max}}$ and intercept equals to $\frac{1}{\mu_{max}}$. The maximum specific growth rate (μ_{max}) of hydrogenesis bacteria grown on POME as substrate was calculated at 0.313 d^{-1} (38 °C). The half-velocity constant (K_s) was 9.04 g/L when POME concentration was 15.0 g/L.

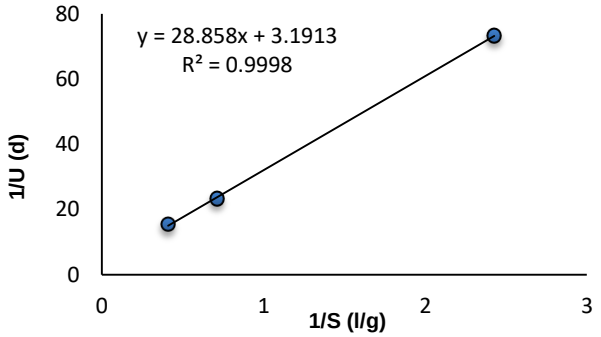

Fig. 1. Line weaver-Burk plot for reciprocals of specific growth rate versus COD concentration.

The maximum specific growth rate of the bacteria is related to the maximum specific substrate utilization rate k according to equation (3).

$$\mu_{max} = kY \quad (3)$$

and

$$k = \frac{\mu_{max}}{Y} \quad (4)$$

where Y is the biomass yield (g $VSS_{produced}$/g $COD_{removed}$). Fig. (2) demonstrated the relationship between specific substrate utilization rate (g COD/g VSS.d) and inverse SRT at different HRT with influent COD concentration of 15000 mg/l. According to Figure (2) slope equals to Y and intercept equals to K_d where K_d is endogenous decay coefficient (g VSS/g VSS.d). In this study, the kinetic parameters Y, K_d, and k were obtained 0.1 g/g, 0.0043 d^{-1}, and 3.13 g COD/g VSS.d, respectively.

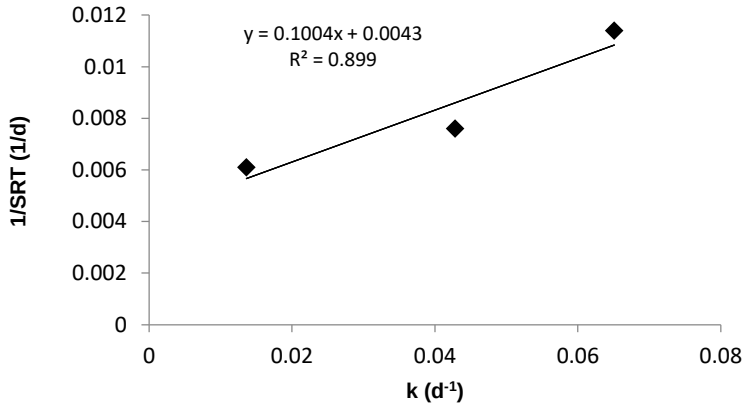

Fig. 2. The reciprocal of SRT versus specific substrate utilization rate.

Table (1) illustrates kinetic coefficients obtained for influent COD concentration of 15000 mg/l used in this study as compared to those reported by Chen *et al.* (2001).

The value of Y (0.1 g/g) obtained in the present study was the identical to that calculated by Chen et al. (2001) for sucrose fermentation in a CSTR. This value is within the reasonable range of anaerobic processes. High K_s value (9.0 g COD/l) showed that the most of the bacteria have low affinity for POME as substrate, due to the reactor being operated at high OLR. The maximum specific microbial growth rate (μ_{max}) is related to the concentration of active biomass in

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the reactor. This relatively high μ_{max} (0.313 d^{-1}) was indicative of the high proportion of active biomass concentration within the reactor (> 20 g/l). The biomass and partially degraded influent VSS made up the total VSS value in the reactor, therefore, it is not an unreasonable expectation that the real μ_{max} value was actually higher.

Table 1. Kinetic parameters for biohydrogen production from POME in different reactors and operating conditions.

Type of reactor	Substrate	S_0 (g /l)	Y g/g	K_s (g/l)	μ_m (d^{-1})	Coefficient basis	Reference
UASB-FF	POME	15.0	0.1	9.0	0.313	COD	This study
CSTR	Sucrose		0.1	0.068	0.172	COD	Chen, (2001)
Serum bottle	molasses	20.0	0.24	0.2	1.32	Sugar	Frascari (2013)

4. Conclusions

Palm oil mill effluent is found to have high Biohydrogen production potential in dark fermentation by a granulated sludge. Monod model following the Line weaver-Burk equation applied to analyse and calculate the kinetic parameters and was found suitable to substrate inhibition and cell carrying capacity in a continuous experiment. The comparatively higher values of maximum specific growth rate, half saturation constant, and biomass yield, 0.313 d-1, 9.04 g/L, and 0.1 g/g, respectively, were obtained at the range of QF and Vup investigated. The experimental results suggest that the formations of all the products were substrate degradation and microbial growth-associated as well substrate degradation for producing VFA was substantially used for hydrogen production.

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