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FEASIBILITY STUDY OF BIOHYDROGEN PRODUCTION FROM PRESSMUD BY UASB PROCESS AND ASSESSMENT OF OPERATING PARAMETERS

RADJARAM B.[1,*]
SARAVANANE R.[2]
SUNDARARAJAN T.[2]

[1]Department of Mechanical Engineering
Manakula Vinayagar Institute of Technology
Puducherry – 605 107, India
[2]Department of Civil Engineering
Pondicherry Engineering College
Puducherry – 605 014, India

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*to whom all correspondence should be addressed:
e-mail: radjaram@rediffmail.com

ABSTRACT

Anaerobic digestion of pressmud diluted with water for biohydrogen production was performed in continuous fed UASB bio reactor for 120 days. Experiment was conducted at a dilution ratio of 1:7.5, by maintaining constant HRT of 30 hrs and the volume of biohydrogen evolved daily was monitored. Various parameters like COD, volatile fatty acid, alkalinity, volatile solids, total and volatile suspended solids and pH with respect to biohydrogen production were monitored at regular interval of time. Specific biohydrogen production rate was 10.98 ml g^{-1} COD reduced /day and 12.77 ml g^{-1} VS reduced on peak yield of biohydrogen. COD reduction was above 70 ± 7%. Maximum gas yield was on the 78th day to 2240 ml day^{-1}. A VSS/TSS of 1-1.5 and VFA/Alkalinity of 0.6 -1.0 were found to be consistent during steady state condition. The aim of the experiment is to study the feasibility of biohydrogen production by anaerobic fermentation of pressmud which is a renewable form of energy to supplement the global energy crisis.

KEYWORDS: Anaerobic digestion, COD, Volatile solids, volatile fatty acid, pH, Alkalinity.

INTRODUCTION

Energy supply of the world's population mostly depends on limited resources of fossil fuels. The utilization of fossil fuels causes global climate change due to emissions of greenhouse gases during their combustion. Hydrogen is a promising energy alternative because it is clean, renewable and has a high energy yield of 2×10^6 kJ m^{-3}. This yield is 2.75-fold greater than that from hydrocarbon fuels. At present, hydrogen is produced mainly from fossil fuels, biomass and water using chemical or biological processes. Hydrogen can be used for power generation and transportation at near zero pollution. The conventional anaerobic treatment process can be divided into two distinct stages: acidification and methane production. Each stage is carried out by a number of microorganisms through syntrophic interactions. Acidification produces H_2 as a by-product, which in turn is used as an electron donor by many methanogens at the second stage of the process. However, H_2 itself is of high commercial value. It can be used as a raw material in a variety of industrial applications as well as a clean energy source for fuel cells. It might be feasible to harvest H_2 at the acidification stage of anaerobic treatment, leaving the remaining acidification products for further methanogenic treatment. The anaerobic conversion of carbohydrates into methane gas is well known. In the case of bio-hydrogen production, the combustion value of carbohydrates is transferred to H_2 gas. As a result, H_2 is more attractive than methane. Anaerobic hydrogen fermenting bacteria can produce hydrogen continuously without the need for photo energy (Ren *et al.,* 1995, Qin *et al.,* 2003). An upflow anaerobic sludge blanket (UASB) process is a widely applied anaerobic treatment system with high treatment efficiency and a short hydraulic retention time (HRT). This work aimed to determine the hydrogen production ability of the biodegradable organic waste viz. pressmud with water.

Table 1. Table of acronym

Acronym	Expansion
COD	Chemical Oxygen Demand
H/D	Height to Diameter Ratio
H2	Hydrogen Gas
HRT	Hydraulic Retention Time
pH	Hydrogen Ion Concentration
SBPR	Specific Biohydrogen Production Rate
TDS	Total Dissolved Solids
TS	Total Solids
TSS	Total Suspended Solids
TVDS	Total Volatile Dissolved Solids
TVSS	Total Volatile Suspended Solids
UASB	Upflow Anaerobic Sludge Blanket
VFA	Volatile Fatty Acid
VS	Volatile Solids
VSS	Volatile Suspended Solids

MATERIALS & METHODS

Bioreactor system

The plexi glass made lab scale UASB reactor (20 l) was used in this study. It has a column of internal diameter 10 cm, height 190 cm (H/D > 10) with a gas liquid separator at the top of internal diameter 20 cm and height 20 cm having an effluent port at 15 cm. The HRT is based on the volume of the fluid between feed and effluent ports which is 20 L. Seven sampling ports were fixed over the entire height of the column at 25 cm gap from the feed port. Total biomass level in the reactor was kept at around 1/3rd the height of the column i.e. about 70 cm. The temperature is kept in ambient condition (30 – 38^0 C) without external heating/cooling and at atmospheric pressure.. The influent pH was kept in the range of 5.5 - 6 by addition of 0.1 N HCl or NaOH. The influent flow rate is controlled by a peristaltic pump to maintain constant HRT of 30 hrs.

Seed micro organism

Sewage sludge contains a variety of microflora favoring biohydrogen production in suspended growth systems (Chen *et al.*, 2001; Chen *et al.*, 2002) and might be a good source for cultivating granular sludge for hydrogen production. The seed sludge was collected from a municipal waste water treatment plant, sieved through wire mesh of diameter 0.5 mm to remove the solid materials. Cow dung was mixed with water in the ratio 1:2 and digested under anaerobic condition for 30 days by adjusting pH in the range of 5-6, in batch mode with the addition of nutrients. Later this cow dung seed was filtered in wire mesh (0.5 mm) to remove the fibrous materials. This cow dung filtrate and sewage was mixed (4:1) heated at 70^0 C for 1 hr to inhibit the methanogens and fed into the reactor. An upward temperature shift could be especially detrimental because it can potentially kill a key digester population. This indicated that the fermentative bacteria which were providing methanogenic substrates, acetate and H2, were the population most inhibited at this temperature. (Zinder *et al.*, 1984; Hisham *et al.*, 2009). This seed was fed into the reactor. The characteristics of seed sludge viz. total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), total volatile solids (TVS), total volatile dissolved solids (TVDS), total volatile suspended solids (TVSS) etc. are given in Table 2.

Table 2 Characteristics of seed and feed

Substrate	pH	TS	TDS	TSS	TVS	TVDS	TVSS	Total COD	Alka-linity	VFA
Seed	6.76	10.9	2.05	8.85	6.8	1	5.8	10.40	19.03	1.82
Feed	6.46	7.7	2.25	5.45	4.65	1	3.65	12.48	12.68	1.50

All units are in g l^{-1} except pH

Feed substrate

So far, majority of research work has been directed at expensive pure substrates to a much lesser quantity of solid waste (Hawkes *et al.*, 2002). In most studies on microbial production of hydrogen, glucose or other pure chemicals were used as a substrate (Das *et al.*, 2001). However, there have been no studies on continuous hydrogen production at enough HRT from organic solid wastes except a few solid and liquid wastes . In this study, pressmud, an organic solid waste of sugar industry is used as substrate for the first time to evaluate the feasibility of biohydrogen production. Pressmud, a semisolid residue from sugar industry, is a byproduct obtained from cane juice before crystallizing sugar. It is the filtered cake from the vacuum filter unit, where the muddy juice is filtered and accumulated pressmud is continuously scraped and collected. It is disposed to farms for feeding as manure without processing, as it is enriched manure for agricultural land.

Operation

The experiment was conducted to investigate the biohydrogen production by mixing pressmud with water. Peristaltic pump (Ravel RH P 100 L) with tube ID ø12 mm was used for pumping feed into reactor.

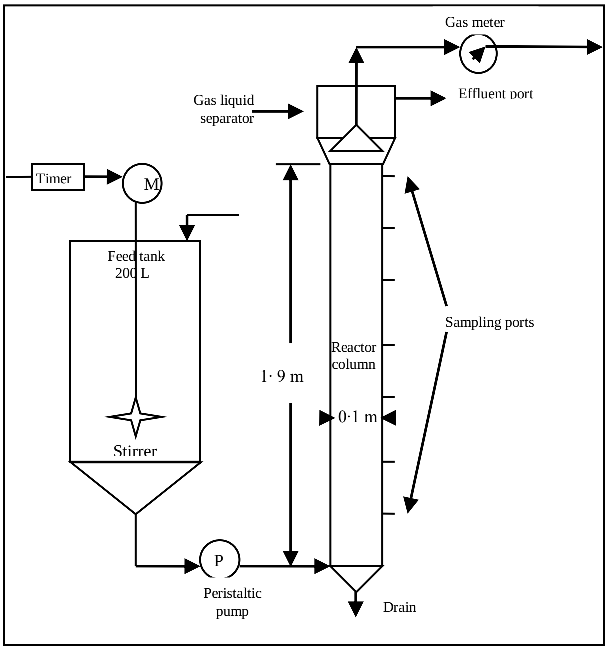

Figure 1. Schematic arrangement of biohydrogen production system

The pressmud being a fibrous material cannot be pumped at low flow rate, as it blocks the pump. Hence it was decided to soak the pressmud in water in the ratio 1:7.5 (4 kg of pressmud with 30 litre water) for 1 hour, filter through wire mesh of 0.5 mm diameter pores to remove the fibrous materials and feed the reactor with this filtrate having particulate mixture of solids less than 0.5 mm only. The feed characteristics were given in Table 1. The filtrate was fed into the feed tank fitted with a mechanical stirrer, which stirs the feed for 3 min at regular time interval of 20 minutes (operated by an electronic timer) to prevent the settlement of solid particles in the tank (Fig. 1)

Analytical methods

Temperature, pH and quantity of biohydrogen yield was measured daily with thermometer, pH probe and gas flow meter (RTI make), while the gas composition was analyzed using gas chromatography (Nucon GC). The total solid, volatile solid (VS), COD, volatile fatty acid (VFA), total suspended solid (TSS), volatile suspended solid (VSS), alkalinity, etc. were estimated once in a week by standard experimental methods (APHA 1995).

RESULTS AND DISCUSSION

Start up of UASB reactor

During the start up period, the reactor was fed continuously with diluted substrate at strength of approximately 10 000 mg COD l^{-1} to reach an OLR of 8,000 to 16,000 g l^{-1} day^{-1}. The pH in the reactor decreased to 5.5 during the start-up period, due to the production of VFA, while biogas production, hydrogen yield and COD removal efficiency gradually increased with time. Biohydrogen production started on the 28th day with an unsteady yield for 76 days. After 76 days both biogas yield and COD removal efficiency stabilized, reaching at approximately 1600 ml/d and 70%, respectively. These results revealed that anaerobic activated sludge in this reactor has possessed a good acid-tolerance and stable hydrogen production ability, which indicated a good acclimatization.

Continuous biohydrogen production

All parameters were tested once in a week from the fourth week until steady state was established. In this study, the steady state was referred to as a relatively stable hydrogen yield of reactor every day with a variation of ± 10%, during which the COD and VS reduction, H_2%, alkalinity, VFA, TSS, VSS were evaluated. The biohydrogen yield was nil in the initial stage for 27 days, production started on 28th day later it was in the range of 100-200 ml day^{-1} till 40th day. The gas generation was between 200-500 ml/day during 40-60 days. It was around 700-800 ml day^{-1} till 70th day. After 70 days the gas yield rose above 1000 ml day^{-1} and was maximum on the 78th day to 2240 ml day^{-1}. After 80 days the production stabilized between 1600-1900 ml day with a fluctuation of ± 10% (Fig. 2.a). This indicates that it requires more than 75 days of start up period for acclimatization, since the feed contains particulate solids suspended in liquid medium.

Biohydrogen yield of 890 ml kg^{-1} pressmud added was achieved in this process at a constant HRT of 30 hrs. Similar studies on wheat feed (Hawkes *et al.,* 2008) fermentation gave 56 l kg^{-1} feed at HRT of 15 hrs and sweet sorgam (Antonopoulou *et al.,* 2008) fermentation gave 10.41 l kg^{-1} feed. Sewage sludge digestion produced biohydrogen of 3.75 ml min^{-1} (Massanet-Nicolau *et al.,* 2008). The feed substrate viz., press mud has 71% water and 29 % total solids in it, i.e., 290 g is effective biomass in 1 kg press mud fed in the reactor. From this about 890 ml of bioH_2 is generated. Moreover, pressmud is a biodegradable organic waste which is used as soil fertilizer only. The H_2% also increased from 10 to 59% from the initial gas generation to the stable range. H_2% was between 52-59 % during steady state condition (Fig. 2.a). From analysis using gas chromatograph, there was no trace of methane. However CO_2 was present in the gas along with hydrogen.

Effect of COD, volatile solid loading rate and % reduction

Hydrogen production from anaerobic fermentation process of organic waste was dependent on COD removal. COD removal fluctuated in the initial startup stage and stabilized after 80 days of operation. COD reduction was between 51 -78 % during the entire period of study. COD reduction between 60-77 % gave consistent gas yield. (Fig.2.b) This high COD reduction is possible due to the large column height (H/D>10) which provides long mixing path way during substrate flow from inlet to outlet. Also the biomass level up to one third the height of the column was able to hold the biohydrogen producing bacteria in the system. This makes the cell to digest the substrate and release the biohydrogen from the reaction process to the maximum possible quantity. Specific biohydrogen production rate (SBPR) was 10.98 ml g^{-1} COD reduced /day for maximum biohydrogen yield. COD reduction was above 70 ± 7%. During consistent gas yield SBPR ranged between 7-11 ml g^{-1} COD reduced/day.(Fig. 2.d)

Anaerobic fermentation of food waste in leaching bed reactor gave biohydrogen yield of 21.2 -41.5 ml/g COD at an HRT of 25 hrs (Kim *et al.,* 2004). biohydrogen yield was 26.13 mol kg^{-1} COD reduced in molasses fermentation (Ren *et al.,* 2006) and 1.8 – 2.3 Mm g^{-1} COD fed in cheese processing waste water (Yang *et al.,* 2007).

The volatile solid concentration of feed increased in the initial stage due to slow hydrolysis in the feed tank. After 30 days, the feed hydrolyzed, particles break up there by steady VS concentration occurred (Fig 2.c). The system was able to take up increased volatile solid loading rate which shows the adaptability of reactor to increased loading without any reduction in efficiency. SBPR was noted as12.77 ml g^{-1} VS reduced on peak yield. Though the SPBR was 32.81 ml g^{-1} VS reduced /day the maximum during the study, it was not stable. SPBR between 10-14 ml g^{-1} VS reduced/day gave consistent biohydrogen yield (Fig. 2.d). A steep increase and decrease in SBPR from 37 – 51 days and 51- 72 days was due to low and high VS loading rates at those periods respectively. Co-digestion of Municipal solid waste and slaughter house waste gave an H_2 yield of 52.5 – 71.3 ml g^{-1} VS reduced (Hejnfelta and Angelidaki, 2009). Maximum specific hydrogen production rate, 9.33 l H_2 g^{-1} VSS d^{-1}, observed in rice winery waste (Yu *et al.,* 2002).

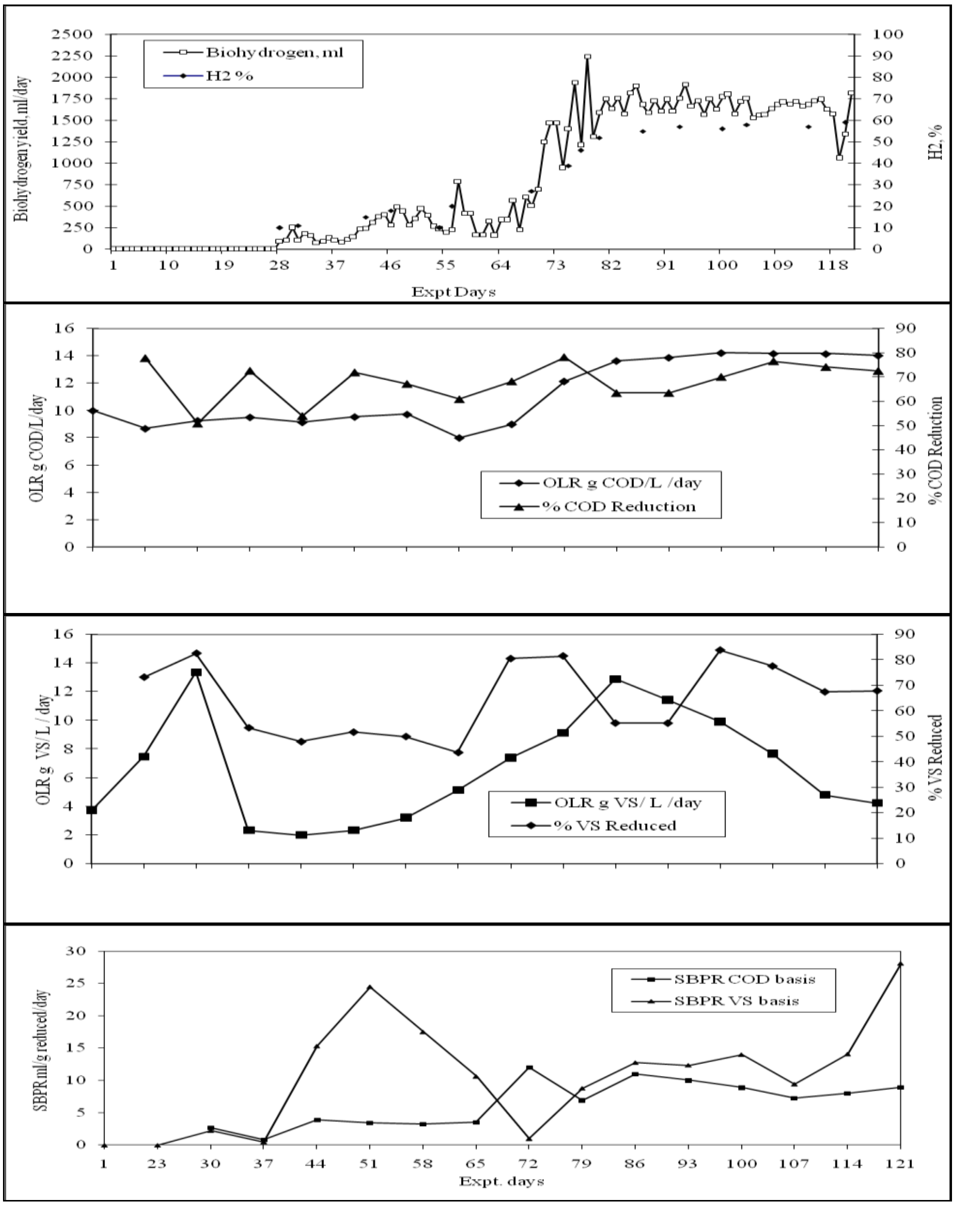

Figure 2. a) Daily bioH_2 yield and %H_2, b) & c) COD & VS loading rate and % reduction d) SBPR for COD and VS reduced Vs Experimental days

VFA, alkalinity and pH variations during biohydrogen production

Anaerobic fermentation is always accompanied by VFA production. The VFA concentration distribution has been used as an indicator for monitoring hydrogen production. As the reactor has an H/D>19, 1.9 times more than the normal UASB reactor, the biomass concentration level increased from the initial level of 15 cm to 120 cm. The dead cells which are light in weight will tend to float and reach the top of reactor. It is found that the sedimentation zone was very thick; the bed zone has a thorough mixing of incoming fresh particles and microorganisms existing in the reactor. The blanket zone is having light weight particles floating in suspended state. Above this is a layer of fluid through which the gas bubbles released by digestion passes and get collected in the gas liquid separator.

The VFA concentration in the effluent was high in the start up stage and reduced gradually showing good indication of acid to hydrogen conversion after 30 days. Later it started increasing after 40 days from start up till 60th days. This is due to the accumulation of the sludge in the reactor. The sludge was removed at the rate of 2 l at port 4 daily. This reduces VFA accumulation in the range below 15000 mg/l. Later this was repeated twice in a week to maintain the VFA level which is the main route for bio hydrogen production. (Fig. 3.a). Before the yield increased above 1000 mg day^{-1} a separation of biomass layer in the reactor occurred at 30 cm from the inlet port. The biomass level was separated by 15 cm gap of liquid. This separation occurred frequently once in every 3 days showing the excellent anaerobic reaction. The separated layer lasted for 4-12 hrs when the particles settle down there by releasing the gas from the packed biomass. Periodical discharge of excess sludge is essential before the maximum sludge holdup is attained (Haandel van and Lettinga, 1994).

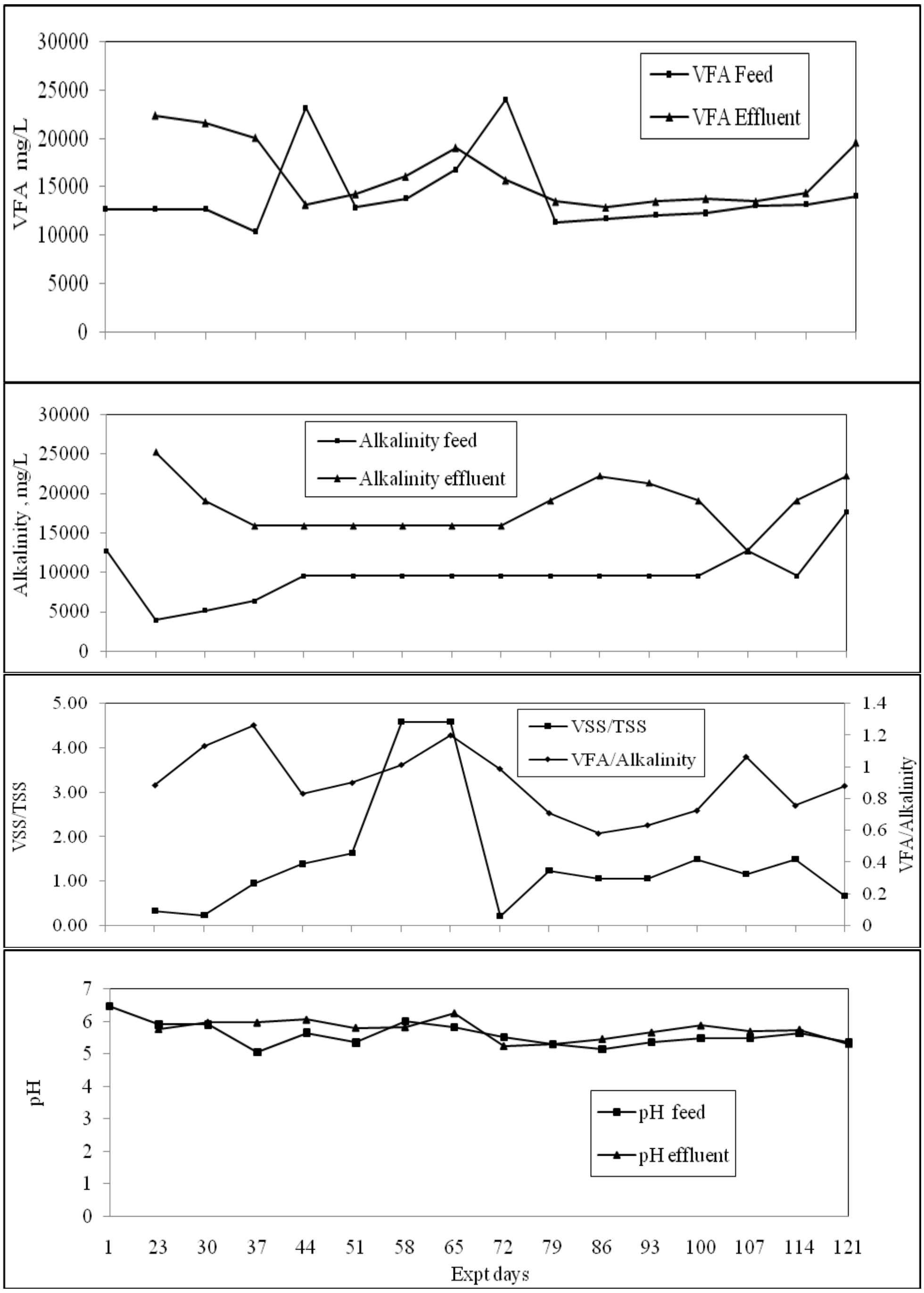

Figure 3. Variations in a) VFA of feed & effluent, b) Alkalinity of feed & effluent, c) VSS/TSS and VFA/Alkalinity ratios of effluent, d) pH of feed and effluent Vs Experimental days

The UASB system is evaluated only based on sludge hold up. A longer HRT reveals more carbohydrates are converted into hydrogen. Ueno (Ueno *et al.* 1995) investigated the hydrogen production rate by anaerobic micro flora in chemostat culture. Their results showed the maximum hydrogen production rate was 198 mmol l^{-1} d^{-1} (4.44 m^3 m^{-3} reactor d^{-1}) and a maximum hydrogen yield of 14 mmol g^{-1} carbohydrate removed (0.63 m^3 kg^{-1} l^{-1} VSS d^{-1})

An increase in the organic loading rate increases alkalinity. The alkalinity was steady during start up period and declined during consistent bio hydrogen yield due to formation of VFA by fermentation process (Fig. 3.b).

The pH of the reactor reduced below 5 during the start up period due to excess volatile fatty acid production, a route of biohydrogen generation. During the entire process the pH was maintained between 5-6. Though the influent pH was kept around 5, the effluent pH tends to rise to 6 during start up. At pH of 5.5 maximum biohydrogen was produced and if pH reached above 6 the biohydrogen yield decreased (Fig. 3.d) Studies on Sucrose in Continuous mode between pH of 3.4–6.3 gave 4.2 as optimum value with maximum hydrogen yield of 1.61 mol mol^{-1} glucose. (Mu *et al.*, 2006) and on Glucose of 4.0–7.0 gave 5.5 as optimum pH with maximum hydrogen yield of 2.1 mol mol^{-1} glucose (Fang and Liu, 2002).

Assessment of VSS/TSS & VFA/Alkalinity ratios

The VSS/TSS ratio in the UASB reactor denotes the organic components of the sludge. Variation in VSS/TSS indicates change in biomass components. A VSS/TSS ratio of 0.6 to 0.8 has been reported in UASB reactor treating sewage (Haandel van and Lettinga, 1994). VSS/TSS ratio was 0.76 for HRT of 24 hours in sucrose treated in UASB reactor (Chang and Lin, 2004). In this study, a VSS/TSS ratio of 1 -1.5 gave maximum biohydrogen yield consistently (Fig. 3.c). An increase in VSS/TSS was noted at 58-65 days due to increased VSS concentration in effluent when gas production started increasing considerably. At very low VSS/TSS ratio, the biohydrogen yield decreased due to high sludge productivity which affects the fermentation process. A low VSS/TSS ratio indicates the organic fraction degradation and sludge mineralization (Lee *et al.*, 2010).

VFA / Alkalinity ratio was 0.6 – 1.0 during consistent gas yield which indicates that a higher alkalinity and lower VFA level in the reactor makes the digestion effective and converts feed to maximum biohydrogen. The concentration of VFA in the feed and reactor effluents showed considerable increase with increasing organic loading rates. To maintain a balanced process, the VFA consumption rate must be equivalent to the production rate to avoid accumulation of VFA. In a properly functioning digester, the alkalinity existing in the digesting sludge neutralizes the excess volatile acids to maintain the pH in the optimum range (Harikishan and Sung, 2003).

CONCLUSIONS

From the experiment conducted for 120 days the following observations were made:

1. COD reduction was above 70 ± 7%.
2. During consistent gas yield SBPR ranged between 7-11 ml g^{-1} COD reduced/day and 10-14 ml g^{-1} VS reduced /day gave consistent biohydrogen yield.
3. The gas yield was maximum on the 78th day to 2240 ml day^{-1}. After 80 days the production stabilized between 1600-1900 ml day^{-1} with a fluctuation of ± 10%. This indicates that it requires more than 75 days of start up period for acclimatization, since the feed contains particulate solids suspended in liquid medium.
4. H_2% was between 52-59 % during steady state condition
5. A VSS/TSS ratio of 1 -1.5 and VFA / Alkalinity ratio was 0.6 – 1.0 gave maximum biohydrogen yield consistently.

It is estimated that biohydrogen yield of 890 ml kg^{-1} pressmud added is possible with this sugar industry waste. As 4% of sugar cane crushed is converted into pressmud, huge amount of biohydrogen production potential is possible which can supplement the global energy crisis and also conserve the fossil fuel and environment

REFERENCES

Antonopoulou G., Gavala H.N., Skiadas I.V., Angelopoulos K. and Lyberatos G. (2008) Biofuels generation from sweet sorghum: Fermentative hydrogen production and anaerobic digestion of the remaining, biomass, *Bioresour Technol*, **99**, 110-119

APHA. (1995) Standard methods for the examination of water and wastewater, 19th ed. New York: American Public Health Association.

Chang F.-Y. and Lin C.-Y., (2004) Biohydrogen production using an upflow anaerobic sludge blanket reactor*, Int J Hydrogen Energy*, **29**, 33 – 39.

Chen C.C., Lin C.Y., Chang J.S. (2001) Kinetics of hydrogen production with continuous anaerobic cultures utilizing sucrose as the limiting substrate, *Appl Microbiol Biotechnol*, **57**, 56–64.

Chen C.C., Lin C.Y., Lin M.C. (2002) Acid-base enrichment enhancement on anaerobic hydrogen production process, *Appl Microbiol Biotechnol*, **58**, 224–228.

Das D., Veziroglu T.N. (2001) Hydrogen production by biological processes: a survey of literature, *Int J Hydrogen Energy* , **26**, 13–28.

Fang H.H.P. and Liu H. (2002) Effect of pH on hydrogen production from glucose by a mixed culture. *Bioresour Technol*, **82,** 87–93.

Haandel van A.C. and Lettinga G. (1994) Anaerobic sewage treatment: a practical guide for regions with a hot climate, London: Wiley, Inc.

Hafez H.; Nakhla G.; El Naggar H. (2009), Biological Hydrogen Production from Corn-Syrup Waste Using a Novel System, *Energies*, **2**, 445 – 455.

Harikishan S. and Sung S., (2003), Cattle waste treatment and Class A biosolid production using temperature-phased anaerobic digester, *Advances in Environmental Research,* **7**, 701–706.

Hawkes F.R., Dinsdale R., Hawkes D.L. and Hussy I., (2002) Sustainable fermentative hydrogen production:challenges for process optimization, *Int J Hydrogen Energy***, 27**, 1339-1347.

Hawkes F.R., Forsey H., Premier G.C., Dinsdale R.M., Hawkes D.L., Guwy A.J., Maddy J., Cherryman S., Shine J. and Auty, (2008) Fermentative production of hydrogen from a wheat flour industry co-product, *Bioresour Technol*, **99**, 5020-5029.

Hejnfelta A. and Angelidaki I., (2009) Anaerobic digestion of slaughterhouse by-products, *Biomass and Bioenergy*, **33**, 1046-1054.

Kim S.-H., Han S.-K. and Shin H.-S., (2004) Feasibility of biohydrogen production by anaerobic co-digestion of food waste and sewage sludge, *Int J Hydrogen Energy*, **29**, 1607-1616.

Lee D.-Y. , Li Y.-Y. and Noike T. , (2010) Influence of solids retention time on continuous H2 production using membrane bioreactor*, Int J Hydrogen Energy*, **35**, 52 – 60.

Massanet-Nicolau J., Dinsdale R. and Guwy A., (2008), Hydrogen production from sewage sludge using mixed microflora inoculum: Effect of pH and enzymatic pretreatment, *Bioresour Technol*, **99**, 6325–6331.

Mu Y., Yu H.Q. and Wang Y. (2006) The role of pH in the fermentative H2 production from an acidogenic granule-based reactor, *Chemosphere*, **64**, 350–358.

Qin Z., Ren N.Q., Li J.Z. and Yan X.F. (2003) Superacid state of acidogenic phase and controlling strategy for recovery, *J Instit Technol*, **35**(9), 1105–1108.

Ren N., Li J., Li B., Wang Y. and Liu S., (2006) Biohydrogen production from molasses by anaerobic fermentation with a pilot-scale bioreactor system, *Int J Hydrogen Energy*, **31**(15), 2147-2157.

Ren N.Q., Wang B.Z. and Ma F. (1995) Hydrogen bio-production of carbohydrate fermentation by anaerobic activated sludge process. Proceedings of the water environment federation annual conference exposure, 68th, p. 145–153.

Ueno Y, Kawai T, Sato S, Otsuka S, Morimoto M. (1995) Biological production of hydrogen from cellulose by natural anaerobic microflora, *J Ferment Bioeng*, **79**(4), 395–397.

Yang P., Zhang R., Mcgarvey J.A., Benemann J. (2007), Biohydrogen Production from Cheese Processing Wastewater by Anaerobic Fermentation Using Mixed Microbial Communities. *Int J Hydrogen Energy*, **32**, 4761-4771.

Yu H., Zhu Z., Hu W. and Zhang H. (2002) Hydrogen production from rice winery wastewater in an upow anaerobic reactor by using mixed anaerobic cultures, *Int J Hydrogen Energy*, **27**, 1359–1365.

Zinder S.H., Anguish T. and Cardwell S.C. (1984), Effects of Temperature on Methanogenesis in a Thermophilic (58°C) Anaerobic Digestor, *Applied and environmental microbiology*, **47**(4), 808-813.