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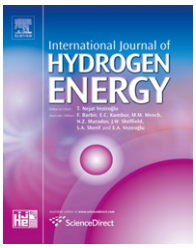

An integrated system for hydrogen and methane production during landfill leachate treatment

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ABSTRACT

The patent-pending integrated waste-to-energy system comprises both a novel bio-hydrogen reactor with a gravity settler (Biohydrogenator), followed by a second stage conventional anaerobic digester for the production of methane gas. This chemical-free process has been tested with a synthetic wastewater/leachate solution, and was operated at 37 °C for 45 d. The biohydrogenator (system (A), stage 1) steadily produced hydrogen with no methane during the experimental period. The maximum hydrogen yield was 400 mL H_2/g glucose with an average of 345 mL H_2/g glucose, as compared to 141 and 118 mL H_2/g glucose for two consecutive runs done in parallel using a conventional continuously stirred tank reactor (CSTR, System (B)). Decoupling of the solids retention time (SRT) from the hydraulic retention time (HRT) using the gravity settler showed a marked improvement in performance, with the maximum and average hydrogen production rates in system (A) of 22 and 19 L H_2/d, as compared with 2–7 L H_2/d in the CSTR resulting in a maximum yield of 2.8 mol H_2/mol glucose much higher than the 1.1–1.3 mol H_2/mol glucose observed in the CSTR. Furthermore, while the CSTR collapsed in 10–15 d due to biomass washout, the biohydrogenator continued stable operation for the 45 d reported here and beyond. The methane yield for the second stage in system (A) approached a maximum value of 426 mL CH_4/gCOD removed, while an overall chemical oxygen demand (COD) removal efficiency of 94% was achieved in system (A).

1. Introduction

Biohydrogen production from organic waste addresses today's two most pressing problems: soaring energy demand and environmental pollution. Microorganisms are capable of producing hydrogen via either photosynthesis or preferably through fermentation [1]. Organic pollutants are anaerobically converted to methane in two distinct stages: acidification and methanogenesis. Acidification produces hydrogen as a by-product which in turn is used as an electron donor by many methanogens at the second stage of the process [2]. Separation of the two stages is feasible for hydrogen collection from the first stage. The second stage is further used for treatment of the remaining acidification products mainly volatile fatty acids.

The continuously stirred tank reactor (CSTR) has been the most widely used system for continuous hydrogen production [3]. Since in a CSTR biomass solids retention time (SRT) is the same as the hydraulic retention time (HRT), the concentration of the mixed liquor suspended solids is highly affected by the short HRT of 3–8 h which is optimal for high hydrogen production rates [3]. The maximum specific growth rate (μ_{max}) for mixed culture of 0.333 h^{-1} [4] corresponds to an SRT_{min} of 3.0 h. However, high dilution rates result in a marked decrease in biomass content in the reactor due to severe cell washout

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and system failure [5]. Decoupling of SRT from HRT in hydrogen bioreactors has been achieved primarily by using biofilms on several media including synthetic plastic media and treated anaerobic granular sludge [6], activated carbon, expanded clay and loofah sponge [7], glass beads [8] and membranes [9]. Problems with the development of methanogenic biofilms on the carrier media adversely impact process stability, which is critical for sustained hydrogen production. Moreover, membranes have not shown many advantages in terms of volumetric hydrogen yield and are also prone to fouling in such a reductive environment.

Extensive literature search using Scifinder Scholar has revealed that the concept of using a gravity settler for decoupling SRT from HRT has not been explored. Thus, in this innovative research, the use of a gravity settler after a hydrogen reactor (Biohydrogenator) [10] for decoupling SRT from HRT through sludge recirculation has been investigated for the first time. In addition, an integrated hydrogen/methane production system is tested for the treatment of synthetic landfill leachate.

2. Materials and methods

2.1. Experimental setup

Two lab-scale systems were operated at 37 °C for 45 d (Fig. 1). Biohydrogenator (system (A)) comprises of a continuously stirred reactor (CSTR) for biological hydrogen production (volume 5 L), CSTR for methane production (volume 10 L), intermediate uncovered gravity settler and storage tank. Since biohydrogen production is optimum at pH of around 5.5–6.5 while anaerobic digestion is optimum at pH 7, $NaHCO_3$ at a concentration of 5 g/L was added to the storage tank to adjust the pH to 7. System (B) consisted of a conventional CSTR for hydrogen production (volume 5 L). Details of the operational conditions including the organic loading rate (OLR) for each system are listed in Table 1. The systems were monitored for total chemical oxygen demand (TCOD), soluble chemical oxygen demand (SCOD), volatile fatty acids (VFAs), ethanol, glucose, volatile suspended solids (VSS), total suspended solids (TSS) and biogas composition including hydrogen, methane and nitrogen. Anaerobically digested sludge from St. Marys wastewater treatment plant, Ontario, was used as the seed. Before startup, a portion of the sludge was preheated to 70 °C for 30 min (to inhibit non spore forming methanogens) as a seed for the hydrogen reactor. The systems were seeded with 5 L of sludge and started up as a continuous system. The feed was a synthetic leachate characterized by: 7.5 g/L of COD consisting mainly of acetic acid 3.5 mL/L, and glucose 3.5 g/L. The feed contained sufficient inorganics: $NaHCO_3$: 3 g/L; $CaCl_2$.0.14 g/L; $MgCl_2.6H_2O$: 0.16 g/L; NH_4HCO_3:0.60 g/L; $MgSO_4.7H_2O$: 0.16 g/L; urea: 1.3 g/L; Na_2CO_3:0.124 g/L; $KHCO_3$:0.156 g/L; K_2HPO_4:0.015 g/L; trace mineral solution: 0.5 g/L; H_3PO_4: 0.44 g/L.

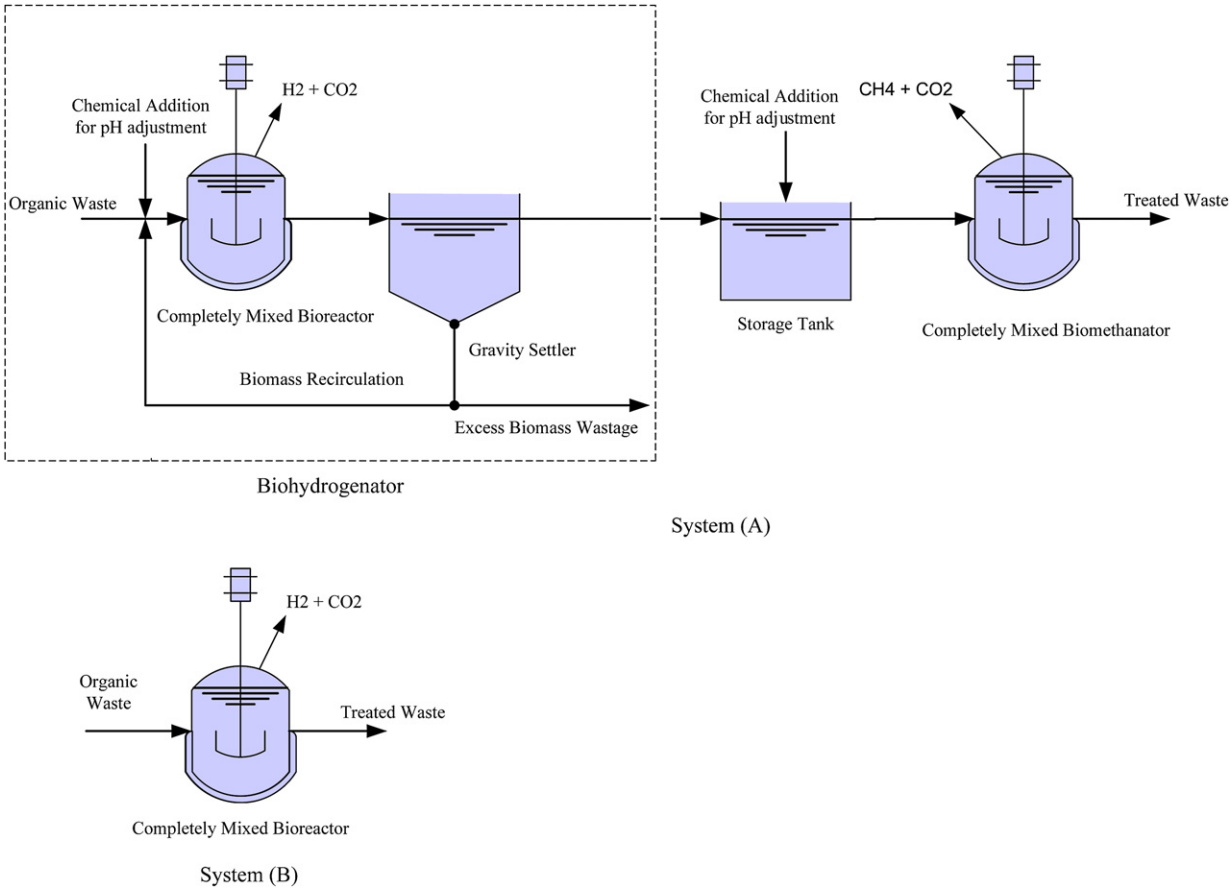

Fig. 1 – Experimental setup.

Table 1 – Operational conditions.

	HRT	SRT	OLR (gCOD/L-d)	pH
System A, Stage (1)	8 h	2.2 d	22.5	5.5–6.5
System A, Stage (2)	10 d	10 d	0.6	6.8–7.2
System B, Run (1)	8 h	8 h	22.5	5.5–6.5
System B, Run (2)	2.2 d	2.2 d	3.4	5.5–6.5

2.2. Analytical methods

The biogas composition including hydrogen, methane and nitrogen was determined by a gas chromatograph (Model 310, SRI Instruments, Torrance, CA) equipped with a thermal conductivity detector (TCD) and a molecular sieve column (Molesieve 5A, mesh 80/100, 6 ft × 1/8 in). Argon was used as carrier gas at a flow rate of 30 mL/min. The temperatures of the column and the TCD detector were 90 and 105 °C, respectively. The concentrations of volatile fatty acids (VFAs) were analyzed using a gas chromatograph (Varian 8500) with a flame ionization detector (FID) equipped with a fused silica column (30 m × 0.32 mm). Helium was used as carrier gas at a flow rate of 5 mL/min. The temperatures of the column and detector were 110 and 250 °C, respectively. A high-performance liquid chromatography system (1200 series, Agilent Technologies) equipped with Aminex HPX-87H ion exclusion column (300 mm × 7.8 mm I.D.; BIO-RAD), and a UV-detector at 210 nm with a refractive index detector (RID) was used to measure the concentrations of glucose and lactate. The temperature of the RID detector was set to 35 °C. The concentrations of volatile suspended solids (VSS) were measured according to standard methods [11]. Total and soluble chemical oxygen demand (TCOD, SCOD) were measured using HACH methods and test kits (HACH Odyssey DR/2500). Soluble parameters were determined after filtering through 0.45 μm filter paper.

2.3. Microbial community analysis

For all biomass samples the total genomic community DNA was extracted using UltraClean Soil DNA Isolation Kit (MO BIO Laboratories, Carlsbad, CA, USA) and after PCR amplification were analyzed by denaturing gradient gel electrophoresis (DGGE). The primer set of 357FGC (5′-CGCCCGCCGCGCGCGGC GGGCGGGGCGGGGGCACGGGGGGCCTACGGGAGGCAGCAG-3′) and 518R (5′-ATTACCGCGGCTGCTGG-3′) at the annealing temperature of 53 °C was used for the PCR amplification of the variable V3 region of 16SrDNA from the purified genomic DNA. Denaturing gradient gel electrophoresis (DGGE) of PCR products was performed with a DCode universal mutation system (Bio-Rad laboratories, Hercules, CA, USA). The PCR products were applied directly to 8% (w/v) polyacrylamide gel with 15–55% denaturant gradients. Electrophoresis was performed at a constant voltage of 130 V at 58 °C for 5 h. The DNA templates of the bands of interest were re-amplified and the PCR products were purified using QIAquick PCR purification Kit (QIAGEN Sciences, Maryland, USA) in accordance with the manufacturer's protocol. The sequences of re-amplified DNA fragments were determined by dideoxy chain termination (Sequencing Facility, John P. Robarts Research Institute, London, Ontario) and compared with available sequences in GenBank database using the BLAST program [12].

3. Results and discussion

3.1. COD degradation

Fig. 2 shows the profile of the chemical oxygen demand (COD) removal efficiency for system (A). The COD removal efficiency was calculated based on the value of the influent and effluent CODs after each stage, and the overall COD removal efficiency was calculated based on the value of the influent and effluent CODs for the overall system. As depicted from the figure during steady state the hydrogen reactor achieved complete glucose degradation, with an average effluent COD of 5484 mg/L and 430 mg/L in stages 1 and 2 respectively. An overall COD removal efficiency of 94% was achieved. The average COD removal efficiency for the biohydrogenator (stage 1) was 28%, while the methane reactor (stage 2) had a COD removal efficiency of 92%. The glucose in the feed was converted mainly to acetate with an average concentration of 870 mg/L and butyrate concentration of 350 mg/L. Table 2 shows the COD mass balance for the biohydrogenator that was closed at 91%. The COD balance included all the liquid products, the hydrogen gas produced and the equivalent COD for the biomass produced. The biomass concentration in the hydrogen reactor was maintained at 2.2 g/L using the recirculation line from the bottom of the gravity settler, which decoupled the solids retention time from the hydraulic retention time, thus increasing the SRT by an approximately 7 folds of the HRT.

3.2. Hydrogen and methane production

Hydrogen production from glucose in dark fermentation produces a stoichiometric yield of 4 and 2 mol H_2/mol glucose according to the two pathways shown below in Eqs. (1) and (2).

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad (1)$$

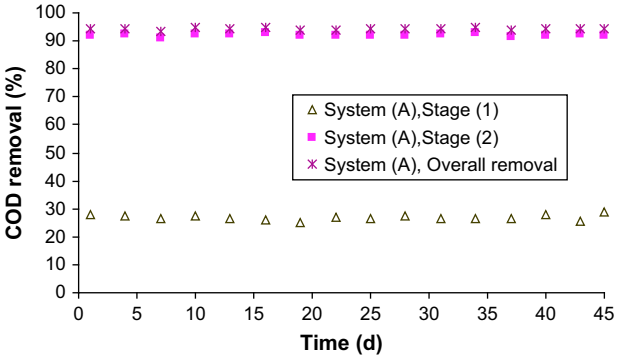

Fig. 2 – Temporal variation of COD removal efficiency.

Table 2 – COD balance for the biohydrogenator.

	Biohydrogenator
VSS (mg/L)	2235 ± 192
VSS out (mg/L)	386 ± 71
VSS out (mgCOD/L)	522 ± 100
SCOD out (mg/L)	5484 ± 72
Acetic (mg/L)	4372 ± 139
Propionic (mg/L)	33 ± 17
Isobutyraic (mg/L)	0
Butyric (mg/L)	354 ± 59
Isovaleric (mg/L)	7 ± 7
Valeric (mg/L)	0
Ethanol (mg/L)	9 ± 4
VFA (mgCOD/L)	5405 ± 88
Glucose Out (mg/L)	0
Hydrogen Gas (L/d)	19 ± 1.7
COD balance (%)	91 ± 2

Note. Values represent average ± standard deviation.

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2 \quad (2)$$

Table 3 summarizes the hydrogen and methane production for the two systems while the temporal variations are illustrated in Figs. 3 and 4. In system (A), the biohydrogenator steadily produced hydrogen with no methane detection for the whole duration of the run. As depicted in Fig. 3, the maximum and average hydrogen production rates (total hydrogen gas in liters per day per reactor volume) in system (A) were 22 and 19 L H_2/d, respectively. The maximum hydrogen yield in the system was 2.8 mol H_2/mol glucose higher than 1.6–2.3 mol H_2/mol glucose reported for continuous-flow reactors [3,13]. Furthermore, the maximum hydrogen yield was 400 mL H_2/g glucose with an average of 345 mL H_2/g glucose, as compared to 141 and 118 ml H_2/g glucose for two consecutive runs that were ran in parallel in system (B). As shown in Fig. 3 a failure in system (B) was observed after 5 d from startup at an HRT of 8 h.

The biomass concentration in the hydrogen reactor at the startup was 5 g VSS/L and decreased to 0.2 g VSS/L at the end of the run due to biomass washout, and glucose degradation efficiency of only 62%. The system was subsequently restarted at an HRT of 2.2 d to mitigate biomass washout, but failed again with biomass concentration decreasing from 7 g/L at startup to 0.5 g/L after 9 d. Moreover, the maximum methane yield for the second stage in system (A) approached 426 mL CH_4/gCOD removed with a methane content of 56% in the biogas produced. To validate the high observed hydrogen yield and to verify the effect of the gravity settler denaturing gradient gel electrophoresis (DGGE) analysis was performed on samples collected from the biohydrogenator effluent and the sludge recirculation stream. DGGE analysis revealed the predominance of the high hydrogen producers *Klebsiella pneumonia*, *Clostridium pasteurianum* and *Clostridium acetobutyricum* and the absence of lactic acid bacteria *Lactobacillus fermentum*.

Table 3 – Summary of hydrogen and methane gas results.

Bioreactor System	Hydrogen gas		Methane gas	
	Content (%)	Yield (mol H_2/mol glucose)	Content (%)	Yield (mL CH_4/g COD)
System A, Stage (1)	43 ± 3.6	2.6 ± 0.2	–	–
System A, Stage (2)	–	–	56 ± 8.1	368 ± 58
System B, Run (1)	25 ± 7.6	1.3 ± 0.8	–	–
System B, Run (2)	11 ± 6.1	1.1 ± 0.5	–	–

Note. Values represent average ± standard deviation.

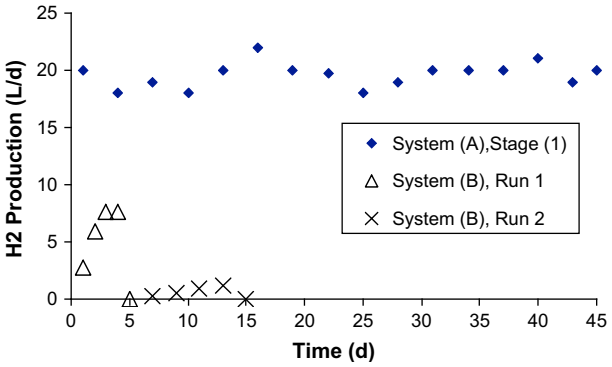

Fig. 3 – Hydrogen production rate.

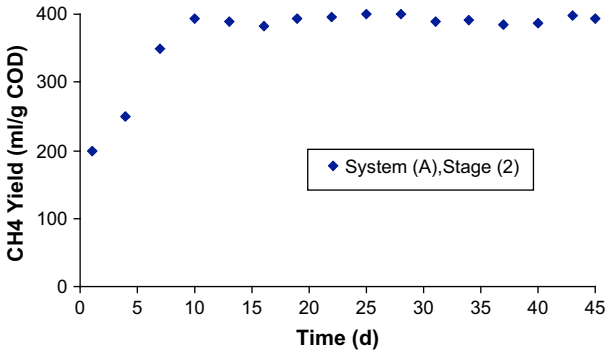

Fig. 4 – Methane yield.

4. Conclusion

In this paper, the benefit of using a gravity settler after a CSTR for hydrogen production was highlighted, by comparing the observed hydrogen yield of 2.8 mol H_2/mol glucose with the yields of 1.3 and 1.1 mol H_2/mol glucose from the conventional CSTR in system (B), and higher than the values of yields reported in the literature. The higher hydrogen yield and the long-term sustainability were achieved primarily due to the decoupling of the SRT from the HRT, which maintained a longer retention time for the biomass in the system and ceased the washout. Moreover, the use of a second stage for methane production was

viable for degrading the products from the first stage and decreasing the effluent COD having an overall COD removal efficiency of 94%, rendering the whole process economically competitive for young landfill leatchate treatment.

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